PB82-242256

SRI International: Assessment of Human Exposures to Atmospheric Acrylonitrile

SRI International
Menlo Park, CA

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Aug 79

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-242256

SRI

Human Exposure To Atmospheric Concentrations Of Selected Chemicals

Office of Air Quality Planning and Standards
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. CRESS Report No. 100	2.	3. RECIPIENT'S ACCESSION NO. PB82 242256
4. TITLE AND SUBTITLE SRI International: Assessment of Human Exposures to Atmospheric Acrylonitrile		5. REPORT DATE August 1979
		6. PERFORMING ORGANIZATION CODE 196002
7. AUTHOR(S) Benjamin E. Suta, Center for Resources and Environmental Systems Studies		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Center for Resource and Environmental Systems Studies		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-02-2835, Task 20
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES Task and Project Officer: Joseph D. Cirvello		

16. ABSTRACT

This report is one in a series that SRI International is providing for the U.S. Environmental Protection Agency to extimate the population-at-risk to selected pollutants. Primarily, this study has sought to estimate environmental exposure of the U.S. population to atmospheric acrylonitrile(AN) emissions. The principal atmospheric sources considered in this report are facilities that produce or that use it as a chemical intermediate.

Many tables included.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Air Quality Standards Air Quality Measurement		EPA 68A

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

SRI International

ASSESSMENT OF HUMAN EXPOSURES TO ATMOSPHERIC ACRYLONITRILE

Final Report

August 1979

By: Benjamin E. Suta
Center for Resource and
Environmental Systems Studies

Prepared for:

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

Task Officer: Joseph D. Cirvello
Project Officer: Joseph D. Cirvello

Contract No. 68-02-2835, Task 20
SRI Project No. CRU-6780
CRESS Report No. 100

2<

333 Ravenswood Ave. • Menlo Park, California 94025
(415) 326-6200 • Cable: SRI INTL MPK • TWX: 910-373-1246

NOTICE

This report has been provided to the U.S. Environmental Protection Agency (EPA) by SRI International, Menlo Park, California, in partial fulfillment of Contract 68-02-2835. The opinions, findings, and conclusions expressed herein are those of the author and are not necessarily those of EPA. Mention of company or product names is not to be considered an endorsement by EPA.

CONTENTS

LIST OF TABLES iv

ACKNOWLEDGMENTS v

I INTRODUCTION 1

II SUMMARY 2

III CHEMICAL AND PHYSICAL PROPERTIES OF ACRYLONITRILE AND ITS ENVIRONMENTAL BEHAVIOR 8

- Introduction 8
- Properties 8
- Environmental Behavior 8

IV ACRYLONITRILE PRODUCTION AND USES 11

- Production 11
- Acrylonitrile Producers and Users 13

V POPULATION EXPOSURES FROM ACRYLONITRILE PRODUCTION . . 16

- Sources of Emissions 16
- Atmospheric Emissions 16
- Atmospheric Concentrations 16
- Exposure Estimates 19

VI POPULATION EXPOSURES FROM PRODUCERS THAT USE ACRYLONITRILE AS A FEEDSTOCK 23

- Sources of Emissions 23
- Atmospheric Emissions 23
- Atmospheric Concentrations 26
- Exposure Estimates 28

VII COMPARISONS OF MONITORING AND DISPERSION MODELING CONCENTRATIONS 30

- General 30
- Atmospheric Monitoring 30
- Comparisons 36

BIBLIOGRAPHY 37

4<

LIST OF TABLES

II-1 Summary of Estimated Population Exposures to Atmospheric Acrylonitrile From Specific Emission Sources 4

II-2 Estimated Acrylonitrile Atmospheric Emissions 7

III-1 Physical Propoerties of Acrylonitrile 9

IV-1 Acrylonitrile Production and Consumption 13

IV-2 AN Producers and Major Consumers 14

IV-3 1977 Use of Acrylonitrile Production Facilities 15

V-1 Emission Factors for Acrylonitrile Production 17

V-2 Estimated Atmospheric Emissions of AN From Monomer Production Facilities 18

V-3 Dispersion Modeling Estimates of Atmospheric Concentrations of Acrylonitrile from Monomer Production 20

V-4 Estimated Human Population Exposures to Atmospheric Acrylonitrile Emitted by Producers 22

VI-1 Estimated Acrylonitrile Emission Rates for ABS/SAN Resin Production 24

VI-2 Estimated Acrylonitrile Emission Rates for Acrylic and Modacrylic Fiber Production 24

VI-3 Estimated Acrylonitrile Emission Rate for Adiponitrile Production 25

VI-4 Estimated Acrylonitrile Emission Rate for Nitrile Elastomer Production 25

VI-5 Dispersion Model Estimates of Omnidirectional Annual Average Acrylonitrile Concentrations[a] ($\mu g/m^3$) for Various Products 27

VI-6 Estimates of Population Exposures to Atmospheric Acrylonitrile Emitted by Plants that use it as a Chemical Intermediate 29

VII-1 Atmospheric Monitoring Data for Acrylonitrile 32

VII-2 Comparison of Monitoring and Dispersion Modeling Data 34

5<

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the cooperation and guidance given by several individuals of the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Joseph Cirvello, Strategies and Air Standards Division, provided direction throughout the study. David Mascone of the Emission Standards and Engineering Division gave valuable assistance in regard to atmospheric emissions. George Schewe and Philip Youngblood of NOAA provided input on atmospheric dispersion modeling.

6<

I INTRODUCTION

This report is one in a series that SRI International is providing for the U.S. Environmental Protection Agency (EPA) to estimate the population-at-risk to selected pollutants. Primarily, this study has sought to estimate environmental exposure of the U.S. population to atmospheric acrylonitrile (AN) emissions. The principal atmospheric sources we consider in this report are facilities that produce or that use it as a chemical intermediate.

7<

II SUMMARY

The annual domestic AN production capacity is approximately 973,000 metric tons. During 1977, the industry operated at 76.6% of capacity, producing 745,000 mt. Future growth of the market is expected to average 6.0-7.5%/yr through 1982, when the demand is estimated to be 850,000-920,000 mt/yr. AN is used primarily as a raw material in the synthesis of other chemicals, in particular for acrylic and modacrylic fiber (45%),* acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins (19%), nitrile elastomers (3%), adiponitrile (10%), acrylamide (3%), nitrile barrier resins (1%), and minor miscellaneous uses (4%). Exports account for approximately 15% of domestic production. Miscellaneous uses include mixing AN with carbon tetrachloride to produce a fumigant for stored tobacco and for equipment used in flour milling and bakery food processing. Although AN is registered as a pesticide in the United States and the EPA has classified it for restricted use by certified applicators, manufacturers have voluntarily withdrawn most pesticides containing AN (IARC, 1979).

AN is a clear, colorless, highly flammable liquid whose characteristic odor is unpleasant and irritating. It boils at 77°C, melts at -83.5°C, and has a specific gravity of 0.8. AN does not react with water and is degraded slowly by both aerobic and anaerobic bacteria. AN is photochemically reactive and has an estimated atmospheric half-life of 9-10 hr. Because AN is a volatile compound, considerable atmospheric discharges from land and water evaporation is expected. This volatility, coupled with a sufficiently long atmospheric half-life, results in aerial transport being a significant mechanism for environmental distribution of AN.

---

*Numbers in parentheses are percents of total domestic production.

8<

Only a few environmental AN atmospheric monitoring data are available from the vicinity of chemical plants. Going (1978) reported on the sampling of atmospheric AN in the vicinity of 11 industrial sites. They placed 4 to 8 monitoring stations at varying directions and distances at each of the 11 sites. Duplicate samples were taken at some stations for quality assurance. They collected samples for only one 24-hr period for 10 of the industrial sites. Two 24-hr samples were collected at the eleventh site. AN was found in the atmosphere at all monitoring stations. The average 24-hr levels for individual station locations ranged from 0.1 to 249 $\mu g/m^3$, with the highest individual 24-hr integrated concentration at 325 $\mu g/m^3$.

Before January 1978, the U.S. Occupational Safety and Health Administration's (OSHA) health standards for exposure to air contaminants required that an employee's exposure to AN not exceed an 8-hr time-weighted average of 20 ppm (45 mg/m^3) in the workplace air in any 8-hr work shift of a 40-hr work week. In January 1978, OSHA announced an emergency standard for AN that limits exposure to an 8-hr time-weighted average of 2 ppm (4.5 mg/m^3) AN in air. A ceiling level of 10 ppm was also set for any 15-min period during the 8-hr shift (IARC, 1979). The occupational standard was finalized at these limits in October 1978.

Nonoccupational human population exposures to atmospheric AN have been estimated for emissions resulting from its production and its use as a chemical intermediate in the production of ABS/SAN resins, acrylic and modacrylic fibers, nitrile elastomer, and adiponitrile. Because of the lack of emission data, exposures were not estimated for acrylamide production. According to Mascone (1979b) the AN emissions from the production of acrylamide are expected to be negligible.

The population exposure estimates are given in Table II-1. The total exposures for each chemical production are summarized both by the total number of people exposed to annual averge concentrations exceeding 0.001 $\mu g/m^3$ and by total risk. We define total risk as the sum of the

9<

Table II-1

SUMMARY OF ESTIMATED POPULATION EXPOSURES TO ATMOSPHERIC ACRYLONITRILE FROM SPECIFIC EMISSION SOURCES

Annual Average AN Concentration[a] ($\mu g/m^3$)	AN Monomer	ABS/SAN Resins	Acrylic and Modacrylic Fibers	Nitrile Elastomer	Adiponitrile
15.0-19.9		2,700			
10.0-14.9	50	--			
5.0-9.9	240	850	4,700	1,800	
1.0-4.9	64,000	73,000	52,000	22,000	
0.50-0.99	140,000	79,000	70,000	81,000	
0.10-0.49	1,800,000	680,000	370,000	650,000	22,000
0.050-0.099	600,000[b]	1,200,000	190,000	690,000	32,000
0.010-0.049	0[b]	1,400,000[b]	260,000[b]	2,700,000[b]	65,000
0.005-0.009	0[b]	510,000[b]	0[b]	5,100[b]	0[b]
0.001-0.004	0[b]	790,000[b]	0[b]	93,000[b]	0[b]
Total people exposed	2,600,000	4,700,000	950,000	4,200,000	120,000
Total risk (person-$\mu g/m^3$	610,000	500,000	270,000	320,000	9,400

---

[a] To convert from $\mu g/m^3$ to ppb, multiply concentrations by 0.46.

[b] Exposures in these ranges are underestimated because calculations were only made for exposures within 30 km of each plant.

10<

number of people exposed to a given concentration times the concentration. Total risk relates directly to cancer mortalities if a linear, no-threshold dose-response function is assumed. We found no human exposures in excess of an annual average of 20 $\mu g/m^3$.

In estimating exposures, we first identified all plants that produce the selected chemicals. EPA (Mascone, 1979a) provided estimates of annual atmospheric AN emissions for each of the plants identified. Dispersion modeling was used to estimate AN concentrations in the vicinity of prototype plants. The emission estimates and source characteristics served as input to atmospheric dispersion models, from which estimates of annual average atmospheric AN concentrations in the vicinity of each plant were obtained. Residential population was estimated for 10 geographical rings about each plant. The ring radii were taken as 0.3-0.5, 0.5-1, 1-2, 2-3, 3-4, 4-6, 6-10, 10-15, 15-20, and 20-30 km. The SRI BESTPOP computer data system, which contains the entire U.S. population on a network of 1-km grids, was used to estimate ring populations. The exposure concentrations were taken as the dispersion modeling estimated annual average concentration at the midpoint of each geographical ring about each plant. Exposure estimates were not made for annual average concentrations of less than 0.001 $\mu g/m^3$. In addition, exposures were not estimated for people residing beyond 30 km from the plants because the dispersion modeling results are considered to be imprecise at the greater distances. Many locations would have had people exposed, beyond 30 km from their plants, to annual average AN concentrations ranging from 0.001 to 0.050 $\mu g/m^3$. Consequently, the reported exposures in this range are underestimated.

Most AN exposures result from ABS/SAN resin and nitrile elastomer production, with more than 4 million people exposed by each. AN monomer production and ABS/SAN resin production result in the highest estimated total risks considering exposed population and exposure concentrations—more than 500,000 person- $\mu g/m^3$ for each.

11<

Table II-2 gives the estimated atmospheric AN emissons from AN monomer production and from its use as a feedstock in other chemicals. We estimate that emissions total about 10,822 mt/yr.

To arrive at these emission and exposure estimates has necessitated reliance on very limited data. Because of the paucity of measured atmospheric AN data, we had to approximate concentrations through the use of dispersion modeling. Moreover, the resulting estimates are subject to considerable uncertainty in regard to: (1) the quantity of AN emissions, (2) AN production and consumption levels, (3) meteorological conditions assumed, (4) control technologies employed, (5) deterioration in control technologies over time, (6) physical characteristics of AN sources (e.g., stack height), (7) details about atmospheric dispersion and degradation, and (8) living patterns of the exposed population. Given these complex variables, the accuracy of the estimates cannot completely be assessed. Comparisons of limited 24-hr monitoring data for 10 locations with dispersion modeling estimates of annual average omnidirectional concentrations shows that, on the average, the monitoring concentrations were about 30% less than the dispersion modeling concentrations. This difference corresponds well with the spiked sampling results, which indicate the average AN recovery for AN monitoring is about 63%.

12<

Table II-2

ESTIMATED ACRYLONITRILE ATMOSPHERIC EMISSIONS

	Emissions (mt/yr)
AN Production	
Absorber vent	537
Flare stack	487
Product loading	136
Fugitive emissions	253
Storage tanks	788
Deep well pond	97
Subtotal	2,298
Production using AN as a feedstock	
Acrylic and modacrylic fibers	4,698
ABS and SAN resins	3,085
Nitrile elastomer	650
Adiponitrile	91
Acrylamide	NE
Subtotal	8,524
Total	10,822

NE = Not estimated, but assumed negligible.

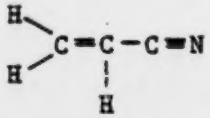
13<

III CHEMICAL AND PHYSICAL PROPERTIES OF ACRYLONITRILE AND ITS ENVIRONMENTAL BEHAVIOR

Introduction

The Chemical Abstracts service registry number for AN is 107-13-1. AN has many synonyms and trade names, including: AN, 2-Propenitrile, cyanoethylene, propenenitrile, VCN, vinyl cyanide, Acrylon, Carbacryl, Fumigrain, and Ventox.

The composition and structure of AN is indicated by the molecular formula, C_3H_3N, and the line diagram,



Properties

An is a clear, colorless liquid whose characteristic odor is unpleasant and irritating. It is moderately soluble in water, soluble in acetone and benzene, and is miscible with ethanol and ether. Other properties are given in Table III-1.

Environmental Behavior

Olefins as a class generally enhance atmospheric oxidation reactions. AN, an olefin, might be expected to participate in these reactions (Miller and Villaume, 1978). Joshi (1977) observed the

Table III-1

PHYSICAL PROPERTIES OF ACRYLONITRILE

Molecular weight	53.06
Melting point, °C	-83.5
Boiling point, °C	77-79
Vapor density	1.8 (air = 1.0)
Specific gravity	0.8004 (25°/4°C)
Vapor pressure	83 mmHg at 20°C 110-115 mmHg at 25°C
Solubility	7.3% by weight in water at 25°C
Exposive limits	3.0-17.0% by volume in air at 25°C
Ignition temperature	481°C
Flash point	-1°C (closed cup)
Conversion factor	1 ppm vapor = 2.17 mg/m^3

Sources: Patterson et al. (1976) and IARC (1979).

photochemical reactivity of AN through the use of a smog chamber. He found acrylonitrile to be reactive with an estimated atmospheric half-life of 9-10 hr. He hypothesized that the products of irradiation of acrylonitrile/NO_x could be: hydrogen cyanide, carbon monoxide, ozone, formaldehyde, and formic acid. Trace amounts of formyl cyanide and nitric acid are also expected.

An atmospheric half-life of 9-10 hr is sufficiently long for aerial transport to play a significant role in the neighborhood distribution of AN. For example, with an average wind speed of 4 m/s, 86% of the emitted AN will survive at 30 km downwind from the source, and 78% will survive at 50 km downwind.

Because AN is a volatile compound and is only moderately soluble in water (7%), it does not react with water. Consequently, it is labeled 0 (no hazard) in the NAS Hazard Rating System for reactivity with water. Hydrogen cyanide is not an expected breakdown product because AN does not dissociate appreciably in water (Miller and Villaume, 1978).

Because the vapor pressure of AN is high, most atmospheric emissions from its manufacture occur as vapor. Because of its only moderate solubility in water, considerable evaporation from land and water emissions into the atmosphere are expected to occur. This volatility, coupled with a sufficiently long atmospheric half-life, results in aerial transport serving as a significant mechanism for environmental distribution of AN.

16<

IV ACRYLONITRILE PRODUCTION AND USES

Production

The annual AN production capacity is approximately 973,000 mt. During 1977, the industry operated at 76.6% of capacity, producing 745,000 mt. Future growth of the market is expected to average 6.0-7.5%/yr through 1982 when the demand is estimated to be 850,000 to 920,000 mt/yr (SRI estimate).

AN is used primarily as a raw material in the synthesis of other chemicals, in particular for acrylic and modacrylic fiber, ABS and SAN resins, nitrile elastomers, adiponitrile, acrylamide, nitrile barrier resins, and other miscellaneous uses. Primary uses of these compounds are as follows:

- Acrylic and modacrylic fibers - More than 60% of these fibers is used in apparel. Carpeting is the second largest use. Home furnishing uses include blankets, draperies, and upholstery. Industrial uses include sandbags, filter cloths, tents, and tarpaulins. The fibers are also used in synthetic hair wigs.
- ABS resin - Its major markets are pipes and pipe fittings and automotive components. Other important markets are large appliances, housing for business machines and telephones, recreational vehicle components, toys, sporting goods, and sheeting material for luggage.

17<

- SAN resin - Its primary uses are for drinking tumblers and other houseware items, for automobile instrument panels, and instrument lenses.
- Nitrile elastomers - Its major uses are in rubber hose, seals, gaskets, latex, adhesives, polyvinyl chloride blending, paper coatings, and pigment binders.
- Adiponitrile - It is hydrogenated to hexamethylenediamine, which is used to produce nylon.
- Acrylamide - Its largest use is in the production of polyacrylamides for waste and water treatment flocculants. Other acrylamide products are used to aid sewage dewatering, and for paper-making strengtheners and retention aids.
- Nitrile barrier resins It is used in the manufacture of beverage containers.
- Miscellaneous uses These uses include the producton of fatty amines and their derivatives, cyanoethylation of various alcohols and amines, fumigation of tobacco, and as an absorbent.

Table VI-1 shows the quantities of AN consumed for these uses. More than 50% of domestic consumption is used in the production of acrylic and modacrylic fibers, and an additional 20% is used in the production of ABS and SAN resins. Exports account for 15% of the total AN production.

18<

Table IV-1

ACRYLONITRILE PRODUCTION AND CONSUMPTION (1977)

	AN (10^3 mt)	Projected Annual Growth (%)[a]
Distribution		
U.S. production	745	NE
Imports	Negligible	NE
Exports	109	NE
Total domestic consumption	636	6.0-7.5
Products		
Acrylic and modacrylic fibers	331	4.5-5.5
ABS and SAN resins	142[b]	7.5-9.5
Nitrile elastomers	24	2.0-3.0
Adiponitrile	73	10.5-12.5
Acrylamide	24	8.0-10.0
Nitrile barrier resins	9	12.0
Other	33	4.0-6.0

NE = Not estimated.

[a] Projected annual average growth until 1982.

[b] 126,000 mt for ABS resin and 16,000 mt for SAN resin.

Source: SRI estimates.

AN Producers and Users

Table IV-2 lists the major AN producers and consumers, along with their estimated installed production capacity as of January 1978. Most of these producers use AN captively at other chemical plants. In fact, during 1976 AN sales acounted for only about 40% of production. The numbers of plants producing AN and its major products follow:

19<

Table IV-2

AN PRODUCERS AND MAJOR CONSUMERS
(January 1, 1978, Production Capacities in Thousands of Metric Tons of AN)

Producer	Location	AN Monomer	Acrylic Fiber	Modacrylic Fiber	ABS Resin	SAN Resin	Nitrile Elastomer and Latex	Adiponitrile	Acrylamide
ABTEC Co.[a]	Louisville, KY				8				
American Cyanamide	Linden, NJ								21
American Cyanamide	Pensacola, FL		49						
American Cyanamide	West Wego, LA	120							7
Borg Warner	Washington, WV				39				
Borg Warner	Ottawa, IL				28	(b)			
Copolymer Rubber	Baton Rouge, LA						2		
Dow	Allyn's Point, CT				8				
Dow	Irontown, OH				8				
Dow	Midland, MI				9	10			18
Dow	Riverside, MO					9			
Dow	Torrance, CA				9				
Dow Badische	Williamsburg, VA		28						
du Pont	Camden, SC		65	3					
du Pont	Beaumont, TX	159							
du Pont	Waynesboro, VA		57						
du Pont	Memphis, TN	122							
Eastman Kodak	Kingsport, TN			7					
B. F. Goodrich	Akron, OH						5		
B. F. Goodrich	Louisville, KY						10		
Goodyear	Akron, OH						1		
Goodyear	Houston, TX						5		
Carl Gorden	Worcester, MA				1				
Mobil Chemical[c]	Joliet, IL				6				
Monsanto	Alvin, TX	200							
Monsanto[d]	Texas City, TX	191							
Monsanto	Decatur, AL		122	9				87	
Monsanto	Addyston, OH				38[e]	7			
Monsanto	Muscatine, IO				15				
Monsanto	Springfield, MA				4				
Nalco	Garyville, LA								4
Uniroyal	Scotts Bluff, LA				24[f]				
Uniroyal	Plainesville, OH						5		
Vistron (SOHIO)[g]	Lima, OH	181	—	—	—	—	—	—	(h)
TOTAL		973	321	19	196	26	28	87	50

---

[a] Jointly owned by Cosden Oil and Chemical and B. F. Goodrich.
[b] Borg Warner plans to build a 55,000-mt ABS plant requiring 15,000 mt of AN at capacity.
[c] Formerly owned by Dart Industries, Rexene Styrene Co.
[d] Capacity is to be increased by 95,000 mt in 1981.
[e] Plans to increase capacity by late 1978 to require an additional 44,000 mt of AN.
[f] Plans to increase capacity by early 1979 to require an additional 23,000 mt of AN.
[g] Includes 45,000 mt older capacity that can be run or placed on standby.
[h] In 1976 Vistron closed a 7,000-mt plant at Lima, OH.

Source: SRI estimates.

Product	Number of Plants
AN	6
Acrylic fiber	5
Modacrylic fiber	3
ABS resin	13
SAN resin	3
Nitrile elastomer	6
Adiponitrile	1
Acrylamide	4

Because many of these plants produce several AN products, 34 plants in all manufacture them.

Chemical producers rarely operate at maximum production capacity for a specific chemical. Table IV-3 shows the percent of production capacities employed in 1977 to produce AN, as well as the major products in which it is used as a feedstock. These percentages range from 48 to 97%.

Table IV-3

1977 USE OF ACRYLONITRILE PRODUCTION FACILITIES
(Thousands of Metric Tons)

Product	AN Capacity[a]	AN Production[b]	% Capacity Used
Acrylic and modacrylic fibers	340	331	97.4
ABS resins	196	126	64.3
SAN resins	26	16	61.5
Nitrile elastomer	28	24	85.7
Adiponitrile	87	73	83.9
Acrylamide	50	24	48.0
Acrylonitrile	973	745	76.6

---

[a] See Table IV-2. This is the amount of AN that would be used annually if production were at 100% of capacity.

[b] See Table IV-1.

V. POPULATION EXPOSURES FROM ACRYLONITRILE PRODUCTION

Sources of Emissions

Table IV-2 lists the AN producers. Their annual plant capacities total 973,000 mt. Table IV-3 indicates that approximately 77% of the production capacity was employed during 1977.

Atmospheric Emissions

Six principal sources of atmospheric AN emissions have been identified for AN production facilities: absorber vents, flare stacks, product loadings, fugitive emissions, storage tanks, and deep well ponds. Incinerators are also a source of emissions, but we did not include them in this analysis because their emission rate is quite low. Table V-1 gives estimated AN emission factors and source descriptions for the six principal emission sources. AN emissions total approximately 1.85 g/kg of product. For each manufacturing plant, Table V-2 gives the estimated emissions resulting from the emission factors. An annual emission of 2,298 mt is estimated for all AN monomer production.

Atmospheric Concentrations

Because atmospheric monitoring data are insufficient (see Section VII), we have employed atmospheric dispersion modeling to estimate atmospheric AN concentrations and their neighboring population exposures. In keeping with the generalized nature of this study, approximate dispersion estimates were made using approximate Gaussian-plume techniques. To facilitate the calculations, the atmospheric dispersion models PTDIS and PTMAX were primarily used for

22<

Table V-1

EMISSION FACTORS FOR ACRYLONITRILE PRODUCTION

Source	AN Emission Factor (g/kg of product)	Source Description
Absorber vent	0.04[a]	Elevated point source[b]
Flare stack	0.50	Elevated point source[b]
Product loading	0.14	Point source at a height of 5 m, no plume rise
Fugitive emissions	0.26	Uniform emissions at a height of 10 m over a 100 m x 100 m area, no plume rise
Storage tanks	0.81	Uniform emissions at a height of 10 m over a 100 m x 100 m area, no plume rise
Deep well pond	0.10	Assumed to be well-controlled

---

[a] The absorber vent emission factor is much larger for American Cyanamide, West Wego (3.0 g/kg), and duPont, Memphis (1.2 g/kg).

[b] We have assumed these to be at an effective stack height of 63 m.

Source: Mascone (1979a and 1979b).

23<

Table V-2

ESTIMATED ATMOSPHERIC EMISSIONS OF AN FROM MONOMER PRODUCTION FACILITIES
(Metric Tons per Year)

Plant/Location	Emission Source						
	Absorber	Flare	Loading[a]	Fugitive	Storage[a]	Pond	Total
American Cyanamide, West Wego, LA	360.8	60.0	16.8	31.2	97.3	12.0	578.0
du Pont, Beaumont, TX	6.4	79.5	22.3	41.3	128.8	15.9	294.2
du Pont, Memphis, TN	146.4	61.0	17.1	31.7	98.8	12.2	367.2
Monsanto, Alvin, TX	8.0	100.0	28.0	52.0	162.0	20.0	370.0
Monsanto, Texas City, TX	7.6	95.5	26.7	49.7	154.7	19.1	353.3
Vistron, Lima, OH	7.2	90.5	25.3	47.1	146.6	18.1	334.8
TOTAL	536.4	486.5	136.2	253.0	788.1	97.3	2,297.5

---

[a] Loading and storage emissions are assumed uncontrolled. Some producers may control up to 90% of these emissions.

Source: Based on data supplied by Mascone (1979a and 1979b).

point sources (absorber vent, flare stack, and product loading) with backup by the single source model CRSTER; the dispersion model PAL (Point-Area-Line) was used for the area sources (fugitive emissions and storage tanks). Table V-1 lists the source parameters used. The meteorological conditions input to the models follow: neutral stability (Pasquill-Gifford "D") and a wind speed of 4 m/s. EPA (Youngblood, 1977) conducted dispersion modeling to estimate the 1-hr downwind concentrations at selected distances from a model plant. These 1-hr average concentrations were adjusted to annual average omnidirectional concentrations (for population exposure assessment) by first dividing them by 20 for conversion to annual maximum values, then further dividing them by 2.5 to smooth the maximum annual values with respect to direction. These factors were derived by Youngblood (1978a) and are based on empirical data and comparisons with more detailed dispersion model results.

We used the dispersion modeling results for each of the six emission sources and the related emission factors in Table V-2 to estimate annual average concentration as a function of distance from a plant that produces 139,700 mt/yr of AN. the estimated atmospheric concentrations from each source type were summed at selected distances from the plant to obtain an estimate of total atmospheric concentrations due to all six emission sources (Table V-3). Because the American Cyanamide plant at West Wego, Louisiana and the duPont plant at Memphis, Tennessee have much larger absorber vent emissions than the other plants, separate estimates for atmospheric AN concentrations resulting from these emissions are given in Table V-3.

Exposure Estimates

The dispersion modeling in Table V-3 is for a model plant producing 139,700 mt/yr of AN, with emissions of 258 mt/yr. Atmospheric AN concentrations around individual plants were estimated by multiplying

Table V-3

DISPERSION MODELING ESTIMATES OF ATMOSPHERIC CONCENTRATIONS OF ACRYLONITRILE FROM MONOMER PRODUCTION

	Annual Average Omnidirectional AN Concentrations ($\mu g/m^3$)		
		Absorber Vent Addition[b]	
Distance from Plant (km)	All Emission Sources[a]	American Cyanamide	duPont
0.4	11.0	0.12	0.05
0.75	5.5	0.59	0.23
1.5	2.4	1.36	0.54
2.5	1.2	1.09	0.43
3.5	0.75	0.80	0.32
5.0	0.46	0.52	0.21
8.0	0.23	0.28	0.11
12.5	0.13	0.16	0.06
17.5	0.08	0.10	0.04
25.0	0.05	0.06	0.03

---

[a] Assumes a plant producing 139,700 mt/yr of AN, with AN emissions of 258 mt/yr. Includes emissions from all six sources listed in Table V-1.

[b] These concentrations are to be added to the estimated concentrations from all other emissions sources. Only two plants are affected: American Cyanamide at West Wego, Louisiana, and duPont at Memphis, Tennessee.

Source: Based on data supplied by Youngblood (1977).

26<

the dispersion modeling concentrations for the model plant by the plant's actual emissions (Table V-2), divided by 258 mt/yr. We then added concentrations resulting from the absorber vent for American Cyanamide, West Wego, and duPont, Memphis, to the estimated concentrations from the other sources.

We estimated exposures for people residing within 10 concentric geographic rings about each plant. The following radii were used: 0.3-0.5, 0.5-1, 1-2, 2-3, 3-4, 4-6, 6-10, 10-15, 15-20, and 20-30 km. We assumed that no one resides within 0.3 km of any plant, since the property boundaries extend at least this far. The estimated annual average AN concentration at the midpoint of each radial ring was taken to represent the exposure concentration for the entire ring.

SRI's computer system, BESTPOP (Suta, 1978) estimated the population residing within the radial distances specified above. The population file consists of a grid of 1-km square sections that span the continental United States. This file was created by assigning the 1960 and 1970 populations to the grid network an by assuming uniform distribution of population within each of 256,000 enumeration districts. The computer software accesses the population file and accumulates residential population within radial rings specified about any given point. in addition, a rectangular map is printed for the area around each specified point to show the population by square kilometer.

Table V-4 gives estimated population exposures to AN from monomer production facilities. We estimate that approximately 2.6 million people are exposed to annual average AN concentrations of 0.05 to 15 $\mu g/m^3$. No population exposure estimates were made for concentrations of less than 0.05 $\mu g/m^3$ because the dispersion modeling was not extrapolated beyond 30 km from any plant and concentration estimates within 30 km were greater than 0.05 $\mu g/m^3$. All AN producers are estimated to cause exposures of 0.001 to 0.05 $\mu g/m^3$ at distances beyond 30 km from their locations.

27<

Table V-4

ESTIMATED HUMAN POPULATION EXPOSURES TO ATMOSPHERIC ACRYLONITRILE EMITTED BY PRODUCERS

Annual Average Atmospheric AN Concentration ($\mu g/m^3$)	Number of People Exposed
10.0-14.9	50
5.0-9.99	240
1.0-4.99	64,000
0.500-0.999	140,000
0.100-0.499	1,800,000
0.050-0.099	600,000[a]
0.010-0.049	0[a]
Total	2,600,000

---

[a] Estimated exposures at this concentration range are underestimated. Correct estimates would have required extrapolating the monitoring data beyond 30 km from each production facility.

A measure of risk was defined as the product of the number of people residing in a geographic ring around a plant times the average AN concentration in that ring. Risk for each plant is the sum of the risks in the 10 concentric rings evaluated. Risk, in units of person-$\mu g/m^3$, for all plants is the sum of the risks for each plant. This measure relates directly to cancer mortalities if a no-threshold, linear dose response relationship is assumed. Total risk for AN emissions from monomer production is estimated to be 610,000 person-$\mu g/m^3$.

28<

VI POPULATION EXPOSURES FROM PRODUCERS THAT USE ACRYLONITRILE AS A FEEDSTOCK

Sources of Emissions

We estimated human population exposures to atmospheric AN from chemical production facilities that use AN as a chemical intermediate. The products we considered are acrylic fibers, modacrylic fibers, ABS resins, SAN resins, nitrile elastomer, adiponitrile, and acrylamide. In some cases the same facility produces several of these chemicals.

Table IV-2 lists the facilities that use AN as an intermediate, their locations, and their capacities. Table IV-3 indicates that, depending on the chemical, from 48% to 97% of the production capacity was used in 1977 for the chemicals noted above.

Atmospheric Emissions

Mascone (1978a) has estimated annual AN atmospheric emissions for plants using AN monomer as a chemical intermediate. These emissions are given in Tables VI-1 through VI-4 for ABS/SAN resin, acrylic and modacrylic fibers, and adiponitrile production. According to Mascone, data about AN emissions for acrylamide production are either unavailable or confidential; nonetheless, he estimates these emissions to be negligible. Consequently, we assume that the population exposures to AN from acrylamide are negligible.

Table VI-1

ESTIMATED ACRYLONITRILE EMISSION RATES FOR ABS/SAN RESIN PRODUCTION

Producer/Location	AN Emissions (mt/yr)
ABTEC, Louisville, KY	125.2
Borg Warner, Washington, WV	1,769.0
Borg Warner, Ottawa, IL	387.4
Dow, Torrance, CA	9.1
Dow, Midland, MI	15.4
Dow, Riverside, MD	5.4
Dow, Allyn's Point, CT	8.2
Dow, Ironton, OH	8.2
Mobile, Joliet, IL	49.9
Monsanto, Addyston, OH	163.3
Monsanto, Muscatine, IA	362.9
Monsanto, Springfield, MA	27.2
Uniroyal, Scotts Bluff, LA	154.2
Total	3,085.0

Source: Mascone (1979a).

Table VI-2

ESTIMATED ACRYLONITRILE EMISSION RATES FOR ACRYLIC AND MODACRYLIC FIBER PRODUCTION

Producer/Location	AN Emissions (mt/yr)
American Cyanamide, Pensacola, FL	90.7
Dow Badische, Williamsburg, VA	725.7[a]
duPont, Camden, SC	479.9
duPont, Waynesboro, VA	338.4
Monsanto, Decatur, AL	2,993.7[a]
Kodak, Kingsport, TN	69.4
Total	4,697.8

---

[a] These plants are currently installing emission controls that should reduce AN emissions by approximately 80% (Mascone, 1979a).

30<

Table VI-3

ESTIMATED ACRYLONITRILE EMISSION RATE FOR ADIPONITRILE PRODUCTION

Producer/Location	AN Emissions (mt/yr)
Monsanto, Decatur, AL	90.7

Source: Mascone (1979a).

Table VI-4

ESTIMATED ACRYLONITRILE EMISSION RATES FOR NITRILE ELASTOMER PRODUCTION

Producer/Location	AN Emissions (mt/yr)
Copolymer Rubber, Baton Rouge, LA	0.9
B. F. Goodrich, Akron, OH	123.4
B. F. Goodrich, Louisville, KY	303.0
Goodyear, Akron, OH	90.7
Goodyear, Houston, TX	78.9
Uniroyal, Plainsville, OH	52.6
Total	649.5

Source: Mascone (1979a).

Atmospheric Concentrations

Because of insufficient atmospheric monitoring data in the vicinities of production plants that use AN as a chemical intermediate (see Section VII), dispersion modeling was used to estimate atmospheric AN concentrations and their neighborhood population exposures. Due to the relatively short stack heights and other source characteristics, the dispersion modeling is primarily based on rough downwind calculations under representative meteorological conditions of neutral (Pasquill "D") atmospheric stability and moderate (4 m/s) wind speed. The 1-hr average downwind concentrations were adjusted to annual average omnidirectional concentrations by first dividing them by 20 for conversion to annual values, then further dividing them by 2.5 to smooth the maximum annual values with respect to direction. These factors were derived by Youngblood (1978a) and are based on empirical data and comparisons with more detailed dispersion modeling results. Table VI-5 gives the results of atmospheric dispersion modeling for acrylic fibers, modacrylic fibers, ABS/SAN resin, and nitrile elastomer production.

ABS/SAN resin plant emissions were assumed to emanate from a 100 m x 100 m area at a height of approximately 17 m. Similarly, the emissions from the modacrylic fiber plant were assumed to emanate from a 100 m x 100 m area at a height of 10 m. Calculations were made for both industries using the PAL computerized dispersion model (Youngblood, 1978b).

The emissions from the nitrile elastomer plants were assumed to emanate from six sources: spray driers, normal driers, liquid rubber, concentrators, recovery, and fugitive emissions (Youngblood, 1978c).

The emissions from the acrylic fiber plant are assumed to emanate from as many as 15 point sources (Schewe, 1978). The dispersion modeling results are given in Table VI-5 for with and without Class "C" stacks because some of the producers do not have these stacks.

32<

Table VI-5

DISPERSION MODEL ESTIMATES OF OMNIDIRECTIONAL ANNUAL AVERAGE ACRYLONITRILE CONCENTRATIONS[a] ($\mu g/m^3$) FOR VARIOUS PRODUCTS

Distance From Plant (km)	Acrylic Fibers Without Class C Stacks[b]	Acrylic Fibers With Class C Stacks[b]	Modacrylic Fibers	ABS and SAN resins	Nitrile Elastomer
0.4	20.5	6.0	27.5	11.5	7.4
0.75	9.6	2.8	11.0	7.5	5.7
1.5	3.6	1.1	3.8	3.3	2.8
2.5	1.7	0.60	1.7	1.6	1.4
3.5	1.0	0.42	1.0	0.96	0.89
5.0	0.60	0.30	0.60	0.59	0.55
8.0	0.30	0.19	0.30	0.29	0.29
12.5	0.16	0.11	0.16	0.15	0.15
17.5	0.10	0.08	0.10	0.10	0.09
25.0	0.06	0.06	0.06	0.06	0.06

---

[a] All concentrations assume a continuous combined annual average AN emission rate of 10 g/s from all sources.

[b] See Schewe (1978) for a description of Class C stacks.

Sources: Based on data given by Youngblood (1978b, 1978c) and Schewe (1978).

33<

Exposure Estimates

The dispersion modeling concentrations given in Table VI-5 are for model plants emitting a total of 10 g/s (315.4 mt/yr) of AN to the atmosphere from all sources. We estimate atmospheric AN concentrations around individual plants by multiplying the appropriate dispersion modeling concentrations for the model plant by the plant's actual emissions (Tables VI-1 through VI-4) and dividing the total by 315.4 mt/yr. We assumed that the emission source characteristics (but not emission rates) for adiponitrile production are similar to those for modacrylic fiber production.

We estimated exposures for people residing within 10 concentric geographic rings about each plant. The following radii were used: 0.3-0.5, 0.5-1, 1-2, 2-3, 3-4, 4-6, 6-10, 10-15, 15-20, and 20-30 km. We assumed that no one resides within 0.3 km of any plant. The estimated annual average AN concentration at the midpoint of each ring was taken to represent the exposure concentration for the entire ring. As we did for AN monomer production plants, we used SRI's computer system BESTPOP (Suta, 1978) to estimate the population residing within the radial distances specified above.

Table VI-6 gives the population exposures to AN from the production of ABS/SAN resins, acrylic and modacrylic fibers, nitrile elastomer, and adiponitrile. Note that because exposures were estimated to only 30 km distance from each plant, very few people were found in the lower exposure concentrations (0.001-0.010 $\mu g/m^3$). It is reasonable to expect that a great number of people are exposed to these concentrations beyond 30 km from the plants.

We defined the measure of risk as the product of the number of people residing in a geographic ring around a plant times the average AN concentration in that ring. Risk for each plant is the sum of the risks in the 10 concentric rings evaluated. Risk for all plants is the sum of the risks for each plant. The units on risk are person-$\mu g/m^3$. This

34<

measure relates directly to cancer mortalities if a no-threshold, linear dose response function is assumed. Total risks are estimated as 500,000 person-$\mu g/m^3$ for ABS/SAN resins, 270,000 person-$\mu g/m^3$ for acrylic and modacrylic fibers, 320,000 person-$\mu g/m^3$ for nitrile elastomers, and 9,400 person-$\mu g/m^3$ for adiponitrile.

Table VI-6

ESTIMATES OF POPULATION EXPOSURES TO ATMOSPHERIC ACRYLONITRILE EMITTED BY PLANTS THAT USE IT AS A CHEMICAL INTERMEDIATE

	Chemical Product			
Annual Average AN Concentration ($\mu g/m^3$)	ABS/SAN Resin	Acrylic and Modacrylic Fibers	Nitrile Elastomers	Adiponitrile
15.0-19.9	2,700			
10.0-14.9				
5.00-9.99	850	4,700	1,800	
1.00-4.99	73,000	52,000	22,000	
0.500-0.999	79,000	70,000	81,000	
0.100-0.499	680,000	370,000	650,000	22,000
0.050-0.099	1,200,000	190,000	690,000	32,000
0.010-0.049	1,400,000[a]	260,000[a]	2,700,000	65,000[a]
0.005-0.009	510,000[a]	0[a]	5,100[a]	0[a]
0.001-0.004	790,000[a]	0[a]	93,000[a]	0[a]
Total People	4,700,000	950,000	4,200,000	120,000
Total Risk	500,000	270,000	320,000	9,400

---

[a] Exposures in these ranges are underestimated because they were only estimated to 30 km from each plant.

VII COMPARISON OF MONITORING AND DISPERSION MODELING CONCENTRATIONS

General

We calculated population exposures by using dispersion modeling to estimate atmospheric AN concentrations. We would have preferred to base the exposure estimates solely on monitoring data; however, few AN monitoring data have been collected in the vicinity of the production plants. It is, nonetheless, of value to compare the dispersion model estimates of atmospheric concentrations with those limited monitoring data to determine if the two are in reasonable agreement with one another.

Atmospheric Monitoring

Going (1978) sampled atmospheric AN in the vicinity of 11 industrial sites. The selected sites included 2 producers of AN, 1 producer of AN and acrylamide, 1 producer of acrylamide, 3 producers of acrylic and modacrylic fibers, 2 producers of ABS and SAN resins, 1 producer of ABS and SAN resins and nitrile elastomers, and 1 producer of nitrile elastomers.

Four to eight monitoring stations were positioned at varying directions and distances from each of the 11 sites. More than one air sampler was deployed at some of the stations as part of the quality assurance program. Samples were collected over one approximate 24-hr period for all stations, except for Monsanto in Decatur, Alabama, where two 24-hr samples were collected.

36<

Quality assurance of the AN sampling program was maintained in three ways. First, blanks were taken to the site and treated as if they were real samples. At least four blanks were used at each site. The AN detected in each of the 16 blank samples analyzed was less than 0.3 μg, which corresponds to the detection limit. Second, duplicate air samples were collected at one or more stations per site, with at least one of the stations downwind of the source. The average difference between the 13 sets of duplicate samples was 20%, with a standard deviation of 25%. Finally, spiked sampling tubes were used at two or more stations per site to establish the actual recovery of AN under real conditions. The average recovery was 63% for the 53 spiked tubes analyzed.

Table VII-1 sets forth the monitoring results. We have averaged the concentrations over duplicate quality assurance samples and over the two 24-hr periods for Decatur. We have estimated the distance that each monitoring station is from the AN producton facilities within a plant. Because some of the plants are fairly large, monitoring stations placed at their boundary can be 0.5 km or more from the AN production facilities.

AN was found in the atmosphere at all monitoring stations at average 24-hr levels for individual stations ranging from 0.1 to 249 $\mu g/m^3$. The highest individual 24-hr concentration was 325 $\mu g/m^3$. Because all sampling was conducted over one or two 24-hr periods, the recorded concentrations depend greatly on the meteorological conditions at the time of sampling, the placement of the monitoring stations, and on the AN production within the plant at the time of sampling.

The elevated concentrations found near the American Cyanamide Plant in Linden, New Jersey, indicate that significant environmental AN emissions may result from the production of acrylamide. We have assumed in the exposure assessments that acrylamide production has negligible AN emission.

Table VII-1

ATMOSPHERIC MONITORING DATA FOR ACRYLONITRILE

Plant/Location	Station Number	Distance[a] (km)	Average AN Concentration[b] ($\mu g/m^3$)
American Cyanamide, New Orleans, LA	1	0.7	<0.1
	2	1.8	<0.1
	3	1.2	<0.1
	4	0.6	12.3 (13.6, 11.0)
	5	0.6	0.4
American Cyanamide, Linden, NJ	1	1.8	0.6(0.6, 0.5)
	2	1.4	15.9
	3	1.3	1.6
	4	1.0	<0.1
	5	1.8	0.7
	6	0.5	0.5
Monsanto Texas City, TX	1	1.5	8.9
	2	2.6	5.2
	3	1.9	2.1
	4	1.6	<0.3
	5	0.8	2.4 (2.2, 2.6)
	6	2.2	0.9
	7	0.7	2.3
Monsanto Decatur, AL	1	5.0	<0.2 (<0.1, <0.2)
	2	1.4	1.8 (4.0, 2.5, <0.3)
	3	1.8	2.3 (4.2, <0.3)
	4	2.2	0.8 (1.6, <0.2, 1.3, 0.2)
	5	1.3	0.6 (0.1,< 0.1, 1.1)
duPont-May Lugoff, SC	1	0.7	0.3
	2	2.1	0.2
	3	1.9	0.2
	4	1.5	0.1
	5	2.2	0.1
	6	1.6	<0.1
	7	1.3	0.3
	8	0.8	1.1
duPont, Waynesboro, VA	1	0.9	<0.2
	2	0.3	7.0
	3	0.4	<0.2 (<0.2, <0.2)
	4	0.7	<0.2
	5	0.5	<0.2
	6	0.5	<0.2

38<

Table VII-1 (Concluded)

Plant/Location	Station Number	Distance[a] (km)	Average AN Concentration[b] (μg/m^3)
Borg-Warner Washington, WV	1	1.3	0.3
	2	0.7	86.1 (99.6, 72.5)
	3	0.5	249.4 (173.7, 325.1)
	4	1.2	<0.2
B. F. Goodrich Louisville, KY	1	0.3	4.3
	2	3.0	<0.2 (<0.2, <0.2)
	3	0.4	<0.2
	4	2.2	<0.2
Monsanto, Addyston, OH	1	0.7	<0.2
	2	0.3	<0.2
	3	1.0	1.1 (1.1, 1.0)
	4	0.7	0.9
	5	0.8	<0.2
Uniroyal, Plainsville, OH	1	0.9	0.9
	2	0.3	3.1
	3	0.7	0.4
	4	0.4	<0.1
	5	0.4	0.7 (0.7, 0.7)
Vistron, Lima, OH	1	0.3	<0.2
	2	0.4	14.5
	3	0.2	16.1
	4	0.3	141.0 (134, 148)
	5	0.6	<0.2

---

[a] Approximate distance from the AN production or use facilities within the plant.

[b] Most concentrations are for one 24-hr period. Some are averaged over duplicate samples taken at the same stations, and some are averaged over two 24-hr periods. Individual values for multiple sampling are shown in parentheses.

Comparisons

Table VII-2 compares the monitoring concentrations and the dispersion modeling concentrations by 0.5-km radial increments around AN plants. The dispersion modeling concentrations are estimated annual omnidirection averages from all sources. They were calculated for the midpoint of each 0.5-km radial increment with the procedures used to estimate population exposures. The monitoring concentrations are the averages over all sampling locations within an 0.5-km radial increment. Thus, each monitoring concentration is the average of one or more sampling station over one or two 24-hr periods.

Because of the differences in the two methods (monitoring and modeling), we cannot expect close agreement between their estimated concentrations. Of the 29 comparisons in Table VII-2, the monitoring and modeling concentrations were equal in one case, the modeling concentrations were larger in 22 cases, and the monitoring concentrations were larger in 6 cases. Overall, the monitoring concentrations were about 30% less than the dispersion modeling concentrations. This difference corresponds well with the spiked sampling results, which indicate that the average recovery for AN monitoring is 63%. That is, the monitoring concentrations are expected to be about 37% less than the actual concentrations due to incomplete AN recovery. Since the modeling concentrations are 30% higher than the monitoring concentrations, estimates based on modeling should be fairly close to actual concentrations.

40<

Table VII-2

COMPARISON OF MONITORING AND DISPERSION MODELING DATA

Plant/Location	Distances[a] (km)	AN Concentration ($\mu g/m^3$)	
		Monitoring[b]	Dispersion[c] Modeling
American Cyanamide	0.50-0.99	4.3	4.3
New Orleans, LA	1.00-1.49	0.1	2.5
	1.50-1.99	0.1	1.9
American Cyanamide	0.50-0.99	0.5	d
Linden, NJ	1.00-1.49	6.0	d
	1.50-1.99	0.7	d
Monsanto	0.50-0.99	2.4	6.5
Texas City, TX	1.00-1.49	nd	---
	1.50-1.99	3.8	2.5
	2.00-2.49	0.9	1.8
	2.50-2.99	5.2	1.3
Monsanto	1.00-1.49	1.2	21.0
Decatur, AL	1.50-1.99	2.3	9.3
	2.00-2.50	0.8	7.2
	2.50-4.99	nd	---
	5.00-5.49	0.2	3.1
duPont-May	0.50-0.99	0.7	7.4
Camden, NJ	1.00-1.49	0.3	2.3
	1.50-1.99	0.1	1.3
	2.00-1.50	0.2	1.1
duPont	0.30-0.49	3.6	5.2
Waynesboro, VA	0.50-0.99	0.2	3.4
Borg-Warner	0.50-0.99	157.6	42.1
Washington, WV	1.00-1.49	0.3	30.4
B. F. Goodrich	0.30-0.49	2.3	7.2
Louisville, KY	0.50-1.99	nd	---
	2.00-2.49	0.2	1.7
	2.50-2.99	nd	---
	3.00-3.49	0.2	1.0

41<

Table VII-2 (Concluded)

Plant/Location	Distances[a] (km)	AN Concentration (μg/m³) Monitoring[b]	AN Concentration (μg/m³) Dispersion[c] Modeling
Monsanto	0.30-0.49	0.2	5.9
Addyston, OH	0.50-0.99	0.4	3.9
	1.00-1.49 1.1	2.8	
Uniroyal	0.30-0.49	1.3	1.2
Plainsville, OH	0.50-0.99	0.7	0.9
Vistron	0.30-0.49	43.4	10.6
Lima, OH	0.50-0.99	0.2	5.2

---

[a] Estimated distance from the AN production within the plant.

[b] Average of all monitoring stations within the indicated distances; all concentrations reported as "less than" (i.e., <) are assumed to be at their upper limit.

[c] Estimated concentrations at the midpoint of the distances.

[d] Dispersion modeling estimates were not made for acrylamide plants.

nd = no data.

42<

BIBLIOGRAPHY

Going, J. E., "Environmental Monitoring Near Industrial Sites: Acrylonitrile," Midwest Research Institute (1978).

International Agency for Research on Cancer, "IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans," Volume 19 (February 1979).

Joshi, S. B., Northrop Services Corp., Letter to J. Cirvello, USEPA, regarding photochemical reactivity of acrylonitrile (July 10, 1977).

Mascone, D. C., EPA, private correspondence (May 24, 1979a).

__________, EPA, personal conversation (May 31, 1979b).

Miller, L. M., and J. E. Villaume, "Investigations of Selected Potential Environmental Contaminants: Acrylonitrile," The Franklin Institute Research Laboratories, EPA 560/2-78-003 (1978).

Patterson, R. M., M. I. Bornstein, and E. Garshick, "Assessment of Acrylonitrile as a Potential Air Pollution Problem," GCA Corporation, GCA-TR-75-32-G(6) (1976).

Schewe, G. J., EPA, memo concerning "Rough Dispersion Estimates of Ambient Acrylonitrile Concentrations from Acrylic Fiber Plants," to J. O'Connor (November 7, 1978).

Suta, B. E., "BESTPOP: A Fine-Grained Computer System for the Assessment of Residential Population," SRI International (1978).

Youngblood, P. L., EPA, memo concerning "Dispersion Modeling for Determining Population Exposures to Benzene," to R. Johnson (January 4, 1978a).

__________, EPA, memo concerning "Rough Estimates of Ambient Concentrations of Acrylonitrile," to J. D. Cirvello (January 26, 1978b).

__________, EPA, memo concerning "Rough Dispersion Estimates for Acrylonitrile from Nitrile Elastomer Plants," to J. O'Connor (September 15, 1978c).

__________, EPA, memo concerning "Rough Estimates of Ambient Concentrations of Acrylonitrile," to J. D. Cirvello (September 22, 1977).

SRI International

July 1978

Final Report

ATMOSPHERIC ETHYLENE DIBROMIDE: A SOURCE-SPECIFIC ASSESSMENT

Prepared for:

Office of Toxic Substances
U.S. Environmental Protection Agency
Washington, D.C. 20460

Project Officer: Vincent J. DeCarlo
Task Officer: Richard J. Johnson

SRI Project 6839

Prepared by:

Susan J. Mara
Shonh S. Lee

Center for Resource and Environmental
Systems Studies Report No. 39

45<

333 Ravenswood Ave. • Menlo Park, California 94025
(415) 326-6200 • Cable: STANRES, Menlo Park • TWX: 910-373-1246

NOTICE

This final report represents the results of work completed in November 1977 and is provided to the U.S. Environmental Protection Agency (EPA) by SRI International, Menlo Park, California, in fulfillment of an agreement with the American Public Health Association. Comments on the draft report (November 1977) were received from EPA in Spring 1978 and have been incorporated into this final report. The opinions, findings, and conclusions expressed here are those of the authors, and not necessarily those of EPA. Mention of company or product names is not to be considered an endorsement by EPA.

CONTENTS

NOTICE iii

LIST OF ILLUSTRATIONS vii

LIST OF TABLES ix

ACKNOWLEDGMENTS xi

I SUMMARY 1

II ETHYLENE DIBROMIDE IN THE ENVIRONMENT 5

- A. Introduction 5
- B. Chemical and Physical Properties 6
- C. General Methodology 8

III CHEMICAL MANUFACTURING AND FORMULATING FACILITIES 11

- A. Sources 11
- B. Methodology 14
- C. Exposures 20

IV GASOLINE SERVICE STATIONS 23

- A. Sources 23
- B. Methodology and Exposures 23

V PETROLEUM REFINERIES 39

- A. Sources 39
- B. Methodology 39
- C. Exposures 44

VI STORAGE AND DISTRIBUTION OF GASOLINE 47

- A. Sources 47
- B. Methodology and Exposures 47

VII URBAN EXPOSURES RELATED TO AUTOMOBILE EMISSIONS 55

- A. Sources 55
- B. Methodology and Exposures 58

BIBLIOGRAPHY 65

APPENDIX - CAPACITIES AND EXPOSED POPULATION BY PETROLEUM REFINERY AND STATE 71

47<

ILLUSTRATIONS

III-1 Commercial Pathways of Ethylene Dibromide 12

III-2 Projected Dispersion Curve for Manufacturing and Formulating Facilities 18

IV-1 Average Concentration of Ethylene Dibromide in Air at 18 Sampling Stations Near a Retail Gasoline Site in Phoenix, Arizona 34

IV-2 Projected Dispersion Curve for Annual Average Concentrations in the Vicinity of Service Stations 35

V-1 Projected Dispersion Curve for Petroleum Refineries 43

VI-1 The Gasoline Marketing Distribution System in the United States 50

VI-2 Vapor and Liquid Flow in a Typical Bulk Terminal 52

VII-1 Isopleths of Mean Annual Wind Speed Through the Morning Mix Layer 59

TABLES

I-1 Summary of Human Exposures to Atmospheric Ethylene Dibromide from Emission Sources 3
II-1 Physical Properties of Ethylene Dibromide 7
III-1 Capacities of Manufacturing and Formulating Facilities . . 13
III-2 Results of Ethylene Dibromide Monitoring in the Vicinity of Manufacturing Facilities 15
III-3 Estimated Population Exposures from Manufacturing and Formulating Facilities 21
IV-1 Self-Service Operations 25
IV-2 Gasoline Market Share of Self-Service Stations in Four AQCRs, Spring 1977 26
IV-3 Gasoline Market Share of Self-Service Stations in Two Metropolitan Areas, 1976. 27
IV-4 Sampling Data from Self-Service Gasoline Pumping 28
IV-5 Estimates of Ethylene Dibromide Exposures from Self-Service Gasoline Pumping 29
IV-6 Service Station Density in Four Metropolitan AQCRs 31
IV-7 Summary of Population Exposed to Ethylene Dibromide from Gasoline Service Stations 37
V-1 Monitoring Data in the Vicinity of Petroleum Refineries . 40
V-2 Estimated Population Exposed to Ethylene Dibromide from Petroleum Refineries 45
VII-1 Automotive Ethylene Dibromide Emission Factors . . . . . .
VII-2 Monitoring Data for Ethylene Dibromide in Urban Areas . . 56
VII-3 Estimates of Average Annual Ethylene Dibromide Concentrations for Cities with Populations Exceeding 1,000,000 61
VII-4 Estimates of Annual Average Ethylene Dibromide Concentrations for Selected SMSAs 63
VII-5 Urban Population Exposures Related to Automotive Emissions 64

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the cooperation and guidance given by several individuals of the U.S. Environmental Protection Agency. Dr. Vincent DeCarlo, Office of Toxic Substances, was project officer. Mr. Richard J. Johnson, Office of Air Quality Planning and Standards, provided vital direction throughout the study. Mr. Phillip L. Youngblood, Office of Air Quality Planning and Standards, provided valuable suggestions about the application of dispersion modeling results to the study of atmospheric ethylene dibromide.

Messrs. Troy P. Miller and Benjamin E. Suta, SRI project supervisors, gave vital support. Mr. Scott W. Dailey edited the report superbly.

50<

I SUMMARY

This report is one in a series that SRI International is preparing on a quick-response basis for the U.S. Environmental Protection Agency (EPA). Populations at risk to selected pollutants are being quantified for input to other, more inclusive studies. This study was undertaken to quantify the environmental exposure of the population to atmospheric emissions of ethylene dibromide (EDB).

Ethylene dibromide is used primarily as a lead scavenger in gasoline. Additional uses include the production of vinyl bromide, soil and space fumigant, production of other plastics, and solvent. There are no known natural sources of the compound.

The five primary sources of atmospheric ethylene dibromide are: chemical manufacturing and formulating facilities, gasoline service stations, petroleum refineries, the storage and distribution of gasoline, and urban exposures related to automobile emissions. Because ethylene dibromide is combusted with gasoline, only evaporative emissions from automobiles have been estimated.

Few quantitative data were available for this study. When data were available, source locations were identified and ethylene dibromide emission rates were estimated. Ambient concentrations of ethylene dibromide were then estimated by applying approximate results of dispersion modeling developed by EPA for an exposure study of benzene, and then extrapolating the results to ethylene dibromide based on differences in vapor pressure and in concentration. Population exposed to concentrations of 1.0 part per trillion (ppt)* and greater were estimated. When data were unavailable, best estimates were developed to provide a reasonable basis for comparison.

---

*The assumed limit of detection.

All estimates presented in the report are subject to considerable uncertainty concerning: (1) the quantity of ethylene dibromide emissions, (2) production and consumption levels of ethylene dibromide, (3) source locations, (4) control technologies employed, (5) deterioration of control technologies over time, and (6) the dispersion characteristics of ethylene dibromide. The estimates, though not precise, provide an approximate estimate of expected conditions.

Table I-1 summarizes the results of the study. Exposures from gasoline service stations and urban exposures related to automobile emissions constitute the two largest sources. Petroleum refineries rank third, exposing more than two million people. Chemical manufacturing and formulating facilities are sources of exposure for more than one million people.

For an approximate comparison of different emission sources, we have calculated exposures in similar units by multiplying the number of people exposed by the annual average concentration of ethylene dibromide within each range. Those values were then summed for each emission source (Table I-1). Thus, the units become "ppt-person-years." For exposures at self-service gasoline stations, an exposure time of 1.5 hours per person per year was assumed.

By far, the most highly-weighted exposures are to people who live in the vicinity of gasoline service stations. Urban exposures related to the evaporation of gasoline from automobiles have the next highest value. Third are chemical manufacturing and formulating, followed by petroleum refineries. These results differ because they are weighted by the number of people exposed to a particular level of atmospheric ethylene dibromide. Thus, they provide a useful basis for comparison and, assuming a linear dose-response relationship, are directly related to human health.

As mentioned previously, the estimates given in this report are subject to considerable uncertainty. Further monitoring and sampling data would be required to improve the accuracy of the analysis. Although the estimated population exposed is substantial, significant reductions in exposures can be expected by 1980 after leaded gasoline is phased out.

Table I-1

SUMMARY OF HUMAN EXPOSURES TO ATMOSPHERIC ETHYLENE DIBROMIDE FROM EMISSION SOURCES

	Population Exposed to Ethylene Dibromide Concentrations (ppt)[a]						
8-Hour Worst Case: Annual Average:	10.0 - 50.0 1.0 - 5.0	50.1 - 100.0 5.1 - 10.0	100.1 - 200.0 10.1 - 20.0	200.1 - 400.0 20.1 - 40.0	> 400.0 > 40.0	Total[b,c]	Comparison Among Sources[c] (10^6 ppt-person-years)
Source							
Manufacturing and Formulating	580,000	250,000	160,000	99,000	84,000	1,200,000	14.0
Gasoline Service Stations							
1. People Using Self-Service					d	30,000,000	1.3
2. People Living in the Vicinity	100,000,000	10,000,000				110,000,000	380.0
Petroleum Refineries	2,000,000	170,000	53,000	16,000	3,000	2,200,000	8.7
Storage and Distribution	e						
Urban Exposures - Automotive	24,000,000					24,000,000	72.0

[a] To convert to $\mu g/m^3$, divide each exposure level by 130.

[b] Population estimates are not additive vertically, because some double counting may exist.

[c] Totals are rounded to two significant figures.

[d] Estimated at 260 ppt for 1.5 hr/yr/person.

[e] Estimated at << 1.0 ppt annual average.

II ETHYLENE DIBROMIDE IN THE ENVIRONMENT

A. Introduction

The primary objective of this study was to quantify the environmental atmospheric exposure of the general population to emissions of ethylene dibromide (EDB). As noted in the summary, this report is one in a series of studies being conducted by SRI for the U.S. Environmental Protection Agency (EPA) to quantify populations at risk to selected pollutants. The studies are generally conducted on a quick-response basis to provide input to other, more inclusive studies. In this project, we identified sources of ethylene dibromide emissions, estimated the resultant atmospheric environmental concentrations of ethylene dibromide, and estimated human populations exposed to various levels of ethylene dibromide concentration. This study has not considered the degree of biological sorption of material. No attempt was required or has been made in this report to assess potential health effects.

Ethylene dibromide is used primarily as an additive in leaded gasoline, a use that accounts for more than 85% of domestic consumption. Ethylene dibromide is used also in vinyl bromide, fumigants, solvent, and other plastics. Although ethylene dibromide has been used in both soil fumigants and commodity and space fumigants, one producer (Dow Chemical USA) has recently ceased marketing its commodity and space fumigant mixture containing the chemical (SRI estimates). Because of the current phasing out of leaded gasoline, production of ethylene dibromide can be expected to fall toward 15% of its estimated current level (Mitre, 1976).

Concern over the possible carcinogenic properties of ethylene dibromide has led the National Institute for Occupational Safety and Health (NIOSH) to issue a new standard for the workplace of no more than 1.0 mg/m^3 (0.13 ppm) of the compound as determined by a 15-minute sampling period. Occupational exposures in ethylene dibromide manufacturing facilities are often above

1.0 mg/m^3 and have been measured as high as 140 mg/m^3 (18 ppm) (Joiner, personal communication, 1977). Generally, the concentrations measured at worksites at which ethylene dibromide is unloaded, transferred, or stored, or where process vessels are being maintained, are consistently higher than samples taken around the manufacturing or blending equipment itself.

Although environmental concentrations of ethylene dibromide are typically three orders of magnitude below occupational levels of exposure, the widespread nature of the emission sources requires that serious attention be given to estimations of environmental exposures.

For this report, five sources of atmospheric ethylene dibromide were considered: manufacturing and formulating; gasoline service stations; petroleum refineries; storage and distribution of gasoline; and urban exposures related to automobile emissions. Because ethylene dibromide undergoes combustion with the gasoline, we have considered only evaporative losses.

B. Chemical and Physical Properties

Ethylene dibromide ($C_2H_4Br_2$; 1,2-dibromoethane) is a dense, colorless, nonflammable liquid that resembles chloroform in odor. The principle physical properties of the compound are shown in Table II-1.

Ethylene dibromide shows a reasonable tendency to degrade in both atmospheric and aquatic receiving environments. The chemical shows a half-life of five to 10 days toward hydrolysis under neutral conditions at ambient temperatures in the aquatic environment (Mitre, 1976). Ethylene dibromide resists atmospheric oxidation by peroxides and ozone, typically showing half-lives in excess of 100 days in those reactions (Mitre, 1976). The compound is generally less reactive in the atmosphere than corresponding alkanes or olefins.

Ethylene dibromide is generally inert at normal temperatures, although slight decomposition may result from exposure to light. It is hydrolyzed to ethylene glycol and bromoethanol at elevated temperature. When heated to 340 to 370C, ethylene dibromide decomposes into vinyl bromide and

Table II-1

PHYSICAL PROPERTIES OF ETHYLENE DIBROMIDE

Chemical Formula	$BrCH_2-CH_2Br$
Molecular Weight	187.88
Boiling Point	131.6C
Melting Point	9.9C
Vapor Pressure, 25C	12 mm
Specific Gravity, liquid	2.17
Specific Gravity, vapor, 25C	6.5
Refractive Index 20C	1.5379
Solubility, water, 20C	4.3 g/l
Solubility, Octanol	∞

Source: Kirk, 1968

hydrobromic acid. The terminal halogen atoms are reactive, making the compound a useful synthetic intermediate. It is the least expensive organic bromine compound available (Mitre, 1976).

Because of a lack of relevant data, it is impossible to assess environmental accumulation of the chemical. It is not known whether rates of atmospheric degradation are sufficient to handle the environmental burden adequately.

C. General Methodology

Few studies have addressed the dispersion of ethylene dibromide in the atmosphere. Little information is available concerning emission factors and precise locations of sources. This study represents a rough approximation of ambient concentrations of ethylene dibromide in the vicinity of sources, and an approximation of exposures to the estimated population. Much of the work was based on a previous SRI study (Mara and Lee, 1977)[*] that evaluated the population exposed to atmospheric benzene. In most cases, it was necessary to rely on dispersion modeling or emission factors developed for benzene sources and to extrapolate to the expected values for ethylene dibromide.

A discussion of the general methodology is warranted. Because evaporation accounts for the major loss of ethylene dibromide to the atmosphere, it is necessary to determine the evaporation rate of the chemical with respect to the evaporation of benzene. It is known that the evaporation rate is proportional to the vapor pressure, solubility, and the molecular weight. Thus, the following equation can be used to estimate the ethylene dibromide emission factor (or emission rate) related to evaporation:

$$\frac{E_a}{E_b} \propto \frac{P_a S_a \sqrt{m_a}}{P_b S_b \sqrt{m_b}} \qquad (2.1)$$

where the subscript a refers to ethylene dibromide and the subscript b refers to benzene; E is the emission rate (or emission factor); P is the vapor pressure; S is the solubility; and m is the molecular weight.

---

[*] This study has subsequently been revised, but the new findings have not been incorporated into this report.

For an estimation, (S) ($\sqrt{m}$) may be approximated by χ, the molar fraction or concentration. Thus, Equation (2.1) can be written as follows:

$$\frac{E_a}{E_b} \propto \frac{P_a \chi_a}{P_b \chi_b} \qquad (2.2)$$

Because the vapor pressures for ethylene dibromide (12 mm) and benzene (100 mm) at room temperature ($\approx$25C) are known, and the volume concentrations of ethylene dibromide (0.05%) and benzene (2.0%) in gasoline are also available, the emission factor (or emission rate) of ethylene dibromide can be estimated by the following equation:

$$E_a = \frac{12}{100} \times \frac{0.05}{2.0} E_b \qquad (2.3)$$

$$E_a = \frac{E_b}{320}$$

This ratio was applied to benzene emission factors related to gasoline emissions in order to estimate comparable factors for ethylene dibromide. When gasoline was not the source of emission(s) the differences in vapor pressure were used alone (i.e., $E_a = 0.12 E_b$).

We emphasize again that few quantitative data were available for this study. All estimates given in the report are subject to a large degree of uncertainty related to the quantity of ethylene dibromide emissions, production and consumption levels of ethylene dibromide, source locations, control technology employed, deterioration of control technology over time, and dispersion modeling. Although the estimates are not precise, they do provide a reasonable evaluation of expected conditions.

III CHEMICAL MANUFACTURING AND FORMULATING FACILITIES

A. Sources

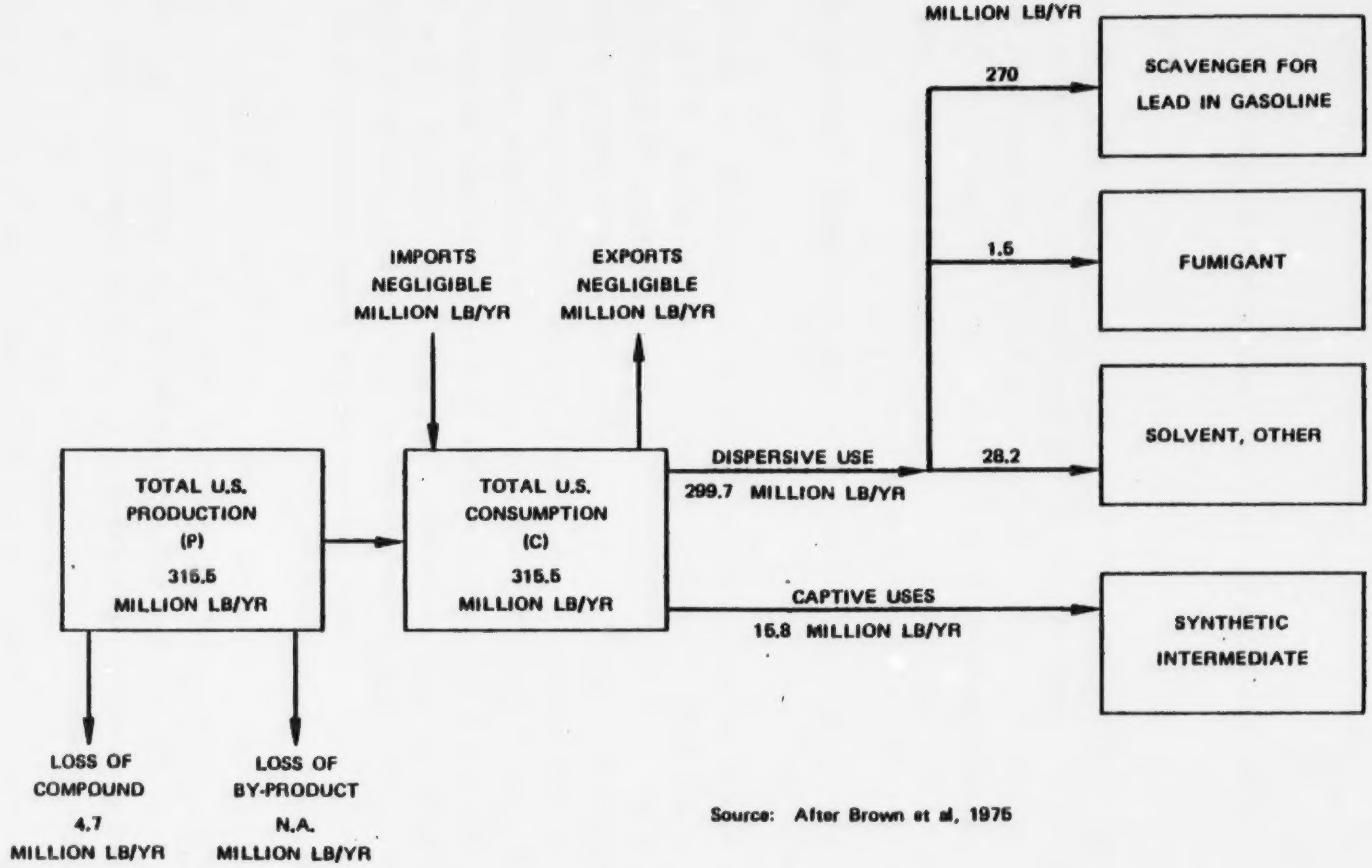
Ethylene dibromide is manufactured in locations that have commercial bromine deposits. Approximately 75% of the production is clustered in the Gulf Coast region of the United States. The capacity for producing ethylene dibromide was approximately 365 x 10^6 lb/yr (168 x 10^6 kg/yr) in 1975 (SRI estimates). Since that time, capacity is estimated to have been reduced only slightly to 350 x 10^6 lb/yr (159 x 10^6 kg/yr).

Approximately 340 x 10^6 lb (154 x 10^6 kg) of ethylene dibromide were sold in 1973 (SRI estimates).

As mentioned earlier, ethylene dibromide is used primarily as a lead scavenger in gasoline. Domestic consumption for that use in 1973 was estimated at 225 x 10^6 lb (102 x 10^6 kg), which represents more than 85% of the compound's consumption. The chemical has shown an annual growth of 3 to 5 percent during the last decade, but as noted previously, consumption is expected to fall off sharply because of the declining use of leaded gasoline. The use of ethylene dibromide as a lead scavenger in gasoline requires blending into an antiknock "motor mix," also known as tetraethyl lead or TEL. The blending takes place at six locations scattered throughout the United States. Figure III-1 shows the commercial pathways of ethylene dibromide in the economy.

Additional uses of ethylene dibromide include the production of vinyl bromide, (5%), fumigant and solvent (10%), and in other plastics (minor market). There are no known natural sources of the chemical. Locations and information on approximate capacity for each manufacturing plant are shown in Table III-1.

Limited monitoring data for two manufacturing facilities were collected by Midwest Research Institute (MRI) in 1975. One air sampling site was


MILLION LB/YR
270
SCAVENGER FOR LEAD IN GASOLINE
1.5
FUMIGANT
28.2
SOLVENT, OTHER
SYNTHETIC INTERMEDIATE
IMPORTS NEGLIGIBLE MILLION LB/YR
EXPORTS NEGLIGIBLE MILLION LB/YR
TOTAL U.S. PRODUCTION (P) 315.5 MILLION LB/YR
TOTAL U.S. CONSUMPTION (C) 315.5 MILLION LB/YR
DISPERSIVE USE 299.7 MILLION LB/YR
CAPTIVE USES 15.8 MILLION LB/YR
LOSS OF COMPOUND 4.7 MILLION LB/YR
LOSS OF BY-PRODUCT N.A. MILLION LB/YR

Source: After Brown et al, 1975

FIGURE III-1. COMMERCIAL PATHWAYS OF ETHYLENE DIBROMIDE

Table III-1

CAPACITIES OF MANUFACTURING AND FORMULATING FACILITIES

Location	EDB Capacity 10^6kg	Production of Vinyl Bromide	Production of Fumigant	TEL Capacity 10^6kg	Estimated EDB use for TEL (10^6kg)
Arkansas					
El Dorado Great Lakes Chemical Corp.	23		x		
Magnolia Dow Chemical Co.	14		x		
Ethyl Corp. (Bromet Co.)	68	x	x		
Total	82				
California					
Antioch E. I. du Pont de Nemours & Co. Inc.				79	14
Louisiana					
Baton Rouge Ethyl Corp				79	14
Michigan					
Midland Dow Chemical Co.	39	x	x		
New Jersey					
Deepwater E. I. du Pont de Nemours & Co. Inc.				79	14
Texas					
Beaumont Houston Chemical Co. (PPG Industries)	16		x	54	10
Freeport Nalco Chemical Co.				18	3
Pasadena Ethyl Corp.				79	14
Total	160			388	69

Source: SRI estimates.

established within 100 m of each plant. The results are shown in Table III-2. Because emission factors were not available, the monitoring data were used to estimate the emission rate at manufacturing facilities. Consequently, the exposure estimates are considered to be crude approximations.

B. Methodology

Each chemical manufacturing and formulating facility may have different production rates, chemical processes, geographic locations, pollution control technology, and meteorological conditions. Thus, detailed dispersion calculations are impractical, given the scope of this study. A simple method of assessment was therefore developed to allow comparative analysis. Variations in geographic locations and meteorological conditions were not considered in the analysis. The results are not precise; rather, they provide a reasonable order-of-magnitude estimate of atmospheric concentrations of ethylene dibromide. A single dispersion curve was projected and applied to all chemical manufacturing and formulating facilities based on previous work done for benzene (Mara and Lee, 1977). The derivation of the methodology is discussed below.

No information on emission factors or characterization of emissions was available for ethylene dibromide manufacturing and formulating facilities. The available monitoring data indicate that emissions are high in comparison to those from other sources. The monitoring data were used as the basis for extrapolation. Rough dispersion modeling of benzene by Youngblood of EPA (1977b) was used and adjusted by monitoring data to project a dispersion curve for ethylene dibromide. The shape of the curve remains approximately the same for ethylene dibromide, but its relative position changes, based on the difference in emission rates.

The general dispersion equation developed by regression analysis is as follows:

$$C = A\,E_A\,D^{-1.48} \tag{3.1}$$

where C is concentration at distance D; A is the system constant, and E_A is the estimated emission rate.

Table III-2

RESULTS OF ETHYLENE DIBROMIDE MONITORING IN THE VICINITY OF MANUFACTURING FACILITIES

Company	Location	Number of Sites[*]	Total Sampling Time (hr)[†]	Concentration (ppb)[‡]	Standard Deviation
Dow	Magnolia, Ark.	1	4	13.2	0.9
Ethyl Corp.	Magnolia, Ark.	1	8	3.1	4.3

---

[*] All sites were within 100 m of the plant.

[†] Samples were discontinuous; two were taken near the Dow facility and five near the Ethyl Corporation facility.

[‡] To convert to μg/m^3, divide by 0.13.

Source: Midwest Research Institute, 1975

The monitoring data for the Dow facility show that the ethylene dibromide concentration at 0.1 km is approximately 100 $\mu g/m^3$ (13 ppb), sampled at a downwind location. (Because the Ethyl Corporation data are highly variable and the sampling site somewhat upwind from the facility, those data were not used in this analysis.) With wind variability considered, 20 $\mu g/m^3$ (3 ppb) is considered to be a reasonable value for the ambient concentration at 0.1 km. Equation (3.1) can be rewritten as follows:

$$C = A' D^{-1.48} \qquad (3.2)$$

where A' is a value representing the product of the system constant and the emission rate. The monitoring data for the Dow facility is then incorporated into Equation (3.2) to solve for A':

$$(20) = A' (0.1)^{-1.48} \qquad (3.3)$$

$$A' = 0.717$$

Thus, Equation (3.2) becomes:

$$C = 0.717D^{-1.48} \qquad (3.4)$$

Rearranging Equation (3.4), it becomes:

$$D = 0.798 \left(\frac{1}{C}\right)^{0.6757} \qquad (3.5)$$

The projected dispersion curve for ethylene dibromide emissions from manufacturing and formulating facilities based on Equation (3.4) and (3.5) is shown in Figure III-2. Because Equation (3.5) and Figure III-2 are based on the production level at the Dow facility, the equation must be normalized to account for varying production rates. The normalized equation can be written as follows:

$$D_i = 0.798 \frac{Pn}{Pd} \left(\frac{1}{C_i}\right)^{0.6757} \qquad (3.6)$$

where C_i is the concentration at distance D_i; and Pn/Pd is the ratio of the production rate at the facility of interest to the Dow production rate (14×10^6 kg/yr).

For uniformity, we have established the ranges of ethylene dibromide concentrations that follow and that apply to all sources:

64<

1.0 - 5.0 ppt
5.1 - 10.0 ppt
10.1 - 20.0 ppt
20.1 - 40.0 ppt
> 40.0 ppt.

For this analysis we used a computer program originally developed to estimate population exposures to benzene (Mara and Lee, 1977). The distance (D_i) at which the specified concentration (C_i) was found was calculated from Equation (3.6). Using the following equation, we then estimated the population that resided within a circle of radius D_i.

$$P_i = d \pi D_i^2 \qquad (3.7)$$

where d is the city or state population density, and P_i is the population exposed to concentration C_i or greater.

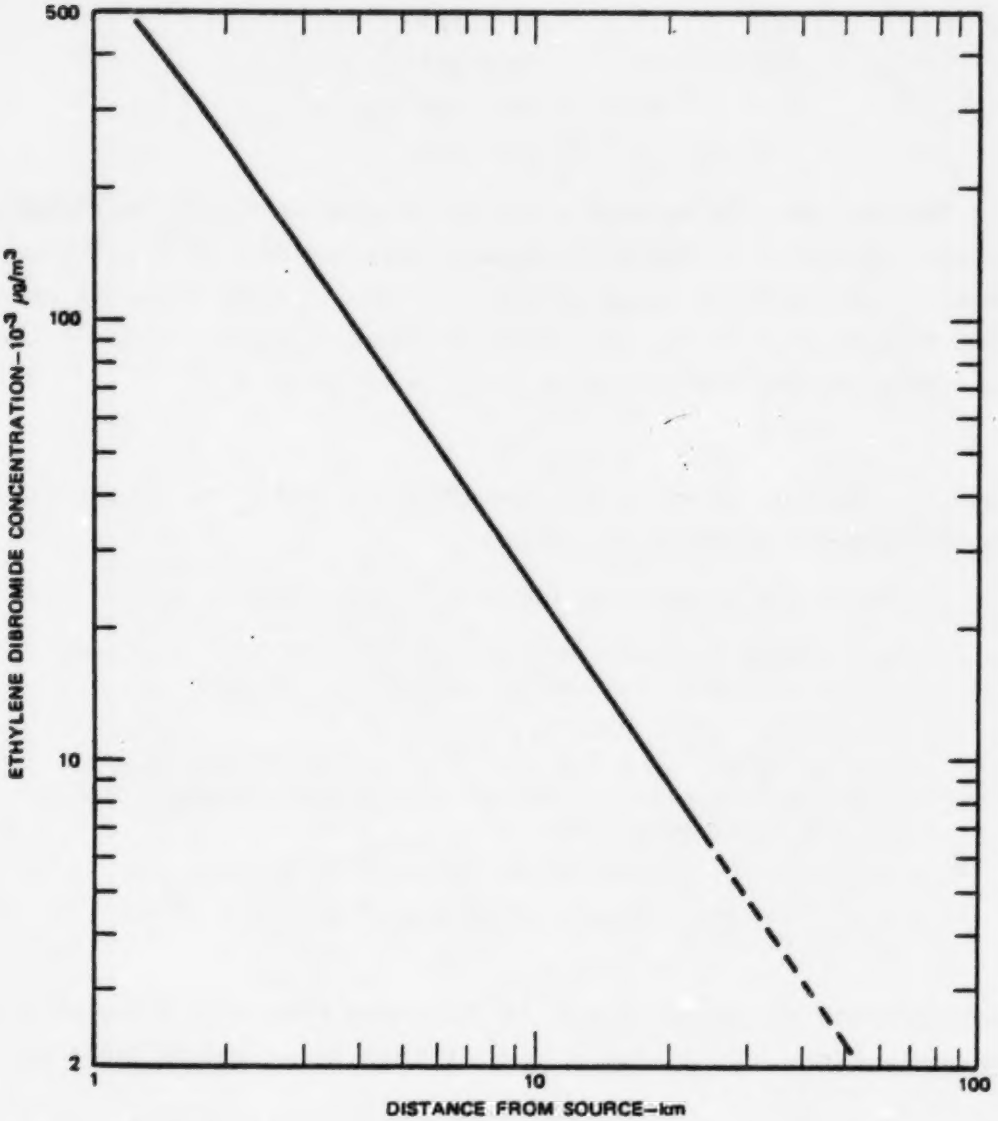
The five main assumptions included in this analysis are:

- The ethylene dibromide source is in the center of the city (if the city has a population greater than 25,000).
- The maximum radius considered is 20 km.
- When a city has more than one plant, it is assumed that these plants are co-located and their corresponding emission rates are summed.
- The population density is uniform over the exposed area.
- If the city has a population of less than 25,000, state density is used.

To accommodate those assumptions, the following steps were included in the computer program. The radius of each city was determined by Equation (3.8):

$$D_c = \left(\frac{P_c}{\pi d_c} \right)^{1/2} \qquad (3.8)$$

where D_c is the estimated radius of the city; P_c is the population of the city (1970 Bureau of Census data); and d_c is the average city density (1970 Bureau of Census data available for cities of population greater than 25,000).



* Based on a production rate of 14 x 10^6 kg/yr (Dow facility)

Source: SRI estimates after Youngblood (1977b)

FIGURE III-2. PROJECTED DISPERSION CURVE* FOR MANUFACTURING AND FORMULATING FACILITIES

When D_i calculated from Equation (3.6) is greater than D_c, or when no city density is available, Equation (3.9) is substituted for Equation (3.7) to calculate the exposed population on the basis of state density.

$$P_i = P_c + d_5 \pi (D_i^2 - D_c^2) \tag{3.9}$$

where d_s is average state population density; D_i is the distance at which concentration C_i is found; D_c is the radius of the city calculated in Equation (3.8); and P_i is the population exposed to concentration C_i or greater. P_c and D_c equal 0 when no city density is available.

The cumulative population totals that resulted were then automatically subtracted, so that the total population within each range of concentrations was printed out. For example, for the range 1.0 to 5.0 ppt, the program subtracted $P_{5.0}$ (a smaller number) from $P_{1.0}$ (a larger number). In other words, $P_{1.0}$ is the population exposed to concentrations of 1.0 ppt or greater. $P_{5.0}$ is the total population exposed to concentrations of 5.0 ppt or greater. By subtracting the two values, the total population exposed to concentrations between 1.0 and 5.0 ppt is determined.

Equation (3.6) requires an estimate of the production or use of ethylene dibromide. Data on capacity were used for ethylene dibromide manufacturing facilities. For tetraethyl lead manufacturers, we multiplied the TEL capacity by 18% (the percentage of ethylene dibromide in TEL) to determine the ethylene dibromide capacity (see Table III-1). Because the same manufacturers produce soil fumigant and vinyl bromide, it was not necessary to make separate estimates for those processes.

The statistics on population were obtained from density data derived from the 1970 census (U.S. Department of Commerce, Bureau of the Census, *1972 County and City Data Book*). When the population density for a city was unavailable, we used the average statewide population density. Although population density in the vicinity of chemical manufacturing plants can vary widely, this method provides a reasonable overall estimate of the exposed population.

C. Exposures

The estimated population exposed to atmospheric ethylene dibromide in the vicinity of chemical manufacturing and formulating facilities is shown in Table III-3. More than one million people are estimated to be exposed to annual average ethylene dibromide concentrations of more than 1.0 ppt, with 30% exposed to annual average levels greater than 10 ppt. The population exposed to the lowest levels may be underestimated because we did not consider concentrations at distances greater than 20 km. At each facility, ethylene dibromide concentrations were estimated to be greater than 1.0 ppt at that distance.

Table III-3

ESTIMATED POPULATION EXPOSURES FROM MANUFACTURING AND FORMULATING FACILITIES

Location	City Density People/km²	State Density People/km²	City Population 10^3	Population Exposed to EDB (ppt)[†] 1.0-5.0	5.1-10.0	10.1-20.0	20.1-40.0	>40.0	Total Exposed Population[‡]
Arkansas									
El Dorado Great Lakes Chemical Corp.	617	15	25	10,000[*]	3,000	1,000	10,000	10,000	34.000
Magnolia Dow Chemical Co. Ethyl Corp. (Bromet Co.) Total	—	15	—	0[*]	8,000[*]	7,000	3,000	2,000	20,000
California									
Antioch E. I. du Pont de Nemours & Co. Inc.	1,481	51	28	60,000[*]	5,000	2,000	10,000	10,000	87,000
Louisiana									
Baton Rouge Ethyl Corp.	1,604	32	166	30,000[*]	70,000	60,000	20,000	20,000	200,000
Michigan									
Midland Dow Chemical Co.	552	61	35	40,000[*]	20,000	10,000	20,000	20,000	110,000
New Jersey									
Deepwater E. I. du Pont de Nemours & Co. Inc.	—	376	—	400,000[*]	40,000	10,000	6,000	4,000	460,000
Texas									
Beaumont Houston Chemical Co. (PPG Industries)	641	18	116	20,000[*]	70,000	30,000	10,000	8,000	140,000
Freeport Nalco Chemical Co	—	18	—	3,000[*]	300	100	40	30	3,500
Pasadena Ethyl Corp.	985	18	89	20,000[*]	30,000	40,000	20,000	10,000	120,000
Total[‡]				580,000	250,000	160,000	99,000	84,000	1,200,000

---

[*] A maximum radius of 20 km was considered in estimating exposed population. Consequently, these estimates may be low because ambient EDB concentrations were above 1.0 ppt at a distance of 20 km.

[†] To convert to μg/m³, divide by 130; to convert to 8-hour worst-case, multiply by 10; rounded to one significant figure.

[‡] Rounded to two significant figures.

Source: SRI estimates.

IV GASOLINE SERVICE STATIONS

A. Sources

Leaded gasoline contains ethylene dibromide as a lead scavenger. The amount of ethylene dibromide added depends upon the lead content of the particular gasoline mix. The 1975 model year was the first in which catalytic converters were required. In that year, 100% of Ford and GM cars and 96% of Chrysler cars required unleaded gasoline. In 1976, approximately 20% of the gasoline sold in the United States was unleaded (Ethyl Corporation, 1976).

The antiknock "motor mix" added to gasoline is a combination of ethylene dibromide, ethylene dichloride, lead, and other alkyl groups. Enough ethylene dichloride is used to supply two atoms of chlorine and enough ethylene dibromide to supply one atom of bromine for each atom of lead. Motor gasoline antiknock mixes typically contain 18.8% ethylene dichloride by weight and 17.9% ethylene dibromide by weight as scavengers.

Whereas the average lead content in all gasoline is 1.5 g/gal, leaded gasoline contains approximately 2.5 g/gal. According to EPA's phase-down schedule for lead, the average lead content for all gasoline will be 0.5 g/gal by 1 October 1979 (Stolpman, personal communication, 1977). Because of the low lead content in unleaded gasoline (approximately 0.01 g/gal), ethylene dibromide is not required and is not added. Therefore, our analysis of population exposures related to gasoline service stations considers only leaded gasoline. The concentration of ethylene dibromide in leaded gasoline is approximately 0.05 percent by liquid volume (Mitre, 1976).

B. Methodology and Exposures

1. Self-Service Operations

Service stations are characterized by their services and business operations; full-service stations, split-island stations, self-service stations, and convenience store operations. In full-service stations, attendants offer all services, including gasoline pumping and other mechanical check-ups. If fuel is obtained at any of the last three classes of stations, the customers may fill up their tanks themselves. In split-island stations, both self-service and full-service are offered. At the two remaining types of stations, only self-service is available. While pumping gasoline, an individual is exposed to ethylene dibromide released as vapor from the gasoline tank.* Although occupants in the car at both self-service and full-service operations are exposed to some degree to ethylene dibromide, the highest exposures are to the person pumping the gas. Because it is difficult to estimate level and length of exposure for occupants, only those who pump gasoline from self-service pumps are considered. (It is not within the scope of this report to evaluate occupational exposures.)

Self-service sale of gasoline is a relatively new marketing method pioneered by independent operators on the West Coast and in the southern United States. Today, it accounts for 30% of gasoline sold. The national market share of the major gasoline producers has decreased recently as independents and others specializing in high-volume, low-margin sales capture a larger percentage. Of the approximately 184,000 conventional service stations and tie-in gasoline operations in the United States, service stations with some self-service operations account for 39% (Arthur D. Little, 1977). Table IV-1 indicates the types of service stations offering self-service gasoline.

---

*Vapor recovery systems can reduce exposure levels significantly, if properly working and operated. Such systems are required for service stations in parts of California.

71<

Table IV-1

SELF-SERVICE OPERATIONS

Outlets Offering Self-Service	Percent of U.S. Total
Total self-service	9%
Split island with self-service	26%
Convenience stores	4%
Total Outlets with Self-Service	39%

Source: Arthur D. Little (1977).

A recent Arthur D. Little report (1977) revealed that 71,300 outlets offer self-service gasoline. Gasoline sold at service stations for the year ending May 30, 1977, equals approximately 87.4 x 10^9 gal in the United States. Of that amount, 27.0 x 10^9 gal (31%) is estimated to have been dispensed at self-service pumps. The market share of self-service stations was surveyed for four metropolitan Air Quality Control Regions (AQCR): Boston, Dallas, Denver, and Los Angeles. The market share held by self-service operations varied from 9% in Boston to 45% in Denver (see Table IV-2). Another study by Applied Urbanetics, Inc. (1976) surveyed Baltimore and Madison, Wisconsin. The results of that study are shown in Table IV-3. It appears that self-service operations account for about 40% of the market in urban areas.

To estimate the people exposed to ethylene dibromide from this source, several assumptions were necessary. The gasoline pumped through self-service outlets is estimated at 27.0 x 10^9 gal. The annual average fuel consumption per vehicle is 736 gal (U.S. Department of Transportation, 1974). If it is assumed that on the average, a person who primarily uses self-service gasoline makes one trip per week to the gasoline station, an average fill-up amount of 14 gal is determined by dividing 736 gal/vehicle/yr by 52 wk/yr. By dividing the average fill-up into the self-service gallons pumped, we estimate trips per year to self-service operations at 1.9 x 10^9. When this number is divided by 52 trips per person per year, the people exposed to pumping self-service gasoline is estimated at 37 x 10^6. We

72<

Table IV-2

GASOLINE MARKET SHARE OF SELF-SERVICE STATIONS IN FOUR AQCRs, SPRING 1977

Type of Operation	Number of Outlets	Sales Volume (10^6 gal/yr)	Market Sharing Percent
Boston AQCR			
Full-service	2,253	1,045.1	91%
Self-service (total)	100	108.6	9
Split island	8[a]		
Self-service	92		
Convenience stores	--		
Dallas AQCR			
Full-service	2,094	924.6	61
Self-service (total)	1,124	593.8	39
Split island	480[a]		
Self-service	444		
Convenience stores	200		
Denver AQCR			
Full-service	621[b]	292.1	55
Self-service (total)	656	235.7	45
Split island	310[a]		
Self-service	226		
Convenience stores	120		
Los Angeles AQCR			
Full-service	2,518	2,472.6	53
Self-service (total)	4,780	2,154.8	47
Split island	3,632[a]		
Self-service	1,022		
Convenience stores	126		

---

[a] Split-island operations offering full service and self-serve islands.

[b] Of these 445 are split island operations that offer full service and mini-serve (attendant-operated) islands.

Source: Arthur D. Little (1977).

Table IV-3

GASOLINE MARKET SHARE OF SELF-SERVICE STATIONS IN TWO METROPOLITAN AREAS, 1976

Type of Operation	Sales Volume (10^6 gal/yr)	Market Sharing Percent
Baltimore SMSA		
Full-service	111.5[a]	55%
Self-service (total)	90.5	45%
Split island	25.5	
Self-service	65.0	
Madison SMSA		
Full-service	56.0[a]	42%
Self-service (total)	77.0	58%
Split island	17.0	
Self-service	60.0	

---

[a] Includes the sales from mini-serve (attendant-operated) stations and 50% of the sales from split islands.

Source: Applied Urbanetics, Inc. (1976).

can further assume that only 80% of these people are pumping leaded gasoline containing ethylene dibromide. Therefore, the number of people exposed from this source is estimated to be 30 x 10^6. This estimate of the population exposed assumes that the individuals using self-service gasoline never obtain gasoline at full-service stations.

Attendants at gasoline service stations were monitored by NIOSH. No samples were above the 0.03 mg analytical level of detection. Therefore, based on the length of sampling periods, concentrations were assumed to be below 30 ppb (Hartle, 1977).

A rough estimate of ethylene dibromide exposures was made by extrapolating the results of benzene monitoring by Battelle (1977). In that study, three samples of ambient air were taken in the breathing zone of persons filling their tanks at self-service gasoline stations. The results, shown in Table IV-4, indicate a wide range in the benzene concentrations of the emissions. The variations seem to be related to the subject's position in relation to the tank opening and the wind direction. Because all measurements were taken on the same day and at approximately the same time, ambient temperature did not cause the variation. Basically, if the subject was downwind of the tank opening, higher levels were recorded. The corresponding ethylene dibromide exposures were estimated based on these data and are presented in Table IV-5.

Table IV-4

SAMPLING DATA FROM SELF-SERVICE GASOLINE PUMPING

Customer	Sampling Rate (mL/min)	Nozzle Time (min)	Gallons Pumped	Sample Volume (L)	Benzene Level	
					$\mu g/m^3$	ppb
1	31	2.5	14	78	115	43
2	31	1.1	8	34	324	121
3	31	1.6	9	50	1740	647

Source: Battelle (1977).

75<

Table IV-5

ESTIMATES OF ETHYLENE DIBROMIDE EXPOSURES FROM SELF-SERVICE GASOLINE PUMPING

Customer	Nozzle Time (min)	Gallons Pumped	Estimated EDB Level $\mu g/m^3$	 ppt
1	2.5	14	0.345	45
2	1.1	8	0.972	126
3	1.6	9	5.220	679

Average Nozzle Time = 1.7 min

Time Weighted Average Exposure = 260 ppt

Source: SRI estimates based on Battelle monitoring data (1977). The conversion is based on differences in vapor pressure and concentration between benzene and ethylene dibromide in gasoline (see Chapter II).

76<

The estimated exposure levels are based on the information contained in Table IV-5. It is recognized that those data are limited and highly variable. However, they do allow a reasonable estimate of expected exposure levels from self-service gasoline pumping. In states where vapor recovery systems are used, the estimated exposure level may be much lower. It can be estimated that approximately 30 x 10^6 persons use self-service stations. While filling their tanks once a week, they are exposed to an estimated ethylene dibromide level of 260 ppt for 1.7 minutes. Their annual exposure is estimated at 1.5 hr. (Table IV-7 summarizes this information.)

2. Vicinity of Service Stations

People residing in the vicinity of service stations are exposed to ethylene dibromide from gasoline evaporation. Ethylene dibromide emissions result from gasoline pumping by attendants and customers, and from gasoline loading by distribution trucks. The amount of ethylene dibromide emitted depends on the ambient temperature, vapor recovery controls, the ethylene dibromide content in gasoline, and the volume of leaded gasoline pumped. Approximately 80% of the gasoline currently sold is leaded. With approximately 184,000 service stations in the United States, it is expected that many people are exposed to ethylene dibromide from those sources. Because density of service stations in urban areas is high and is expected to correlate well with urban population density, only urban areas are considered in this analysis.

An emission factor of 0.00157 g/g/lead/gal from refueling losses has been estimated based on testing at EPA's Mobile Source Air Pollution Control Laboratory in Ann Arbor, Michigan (Kittredge, 1977). The factor considers spilling, vapor displacement, entrained liquid gasoline losses and volume of gasoline pumped. Assuming an average lead content in gasoline of 2.5 g/gal, the estimated emission factor for ethylene dibromide is 0.00039 g/gal.

The number of service stations in urban areas can be estimated based on service station density and total U.S. population in urban areas. Service station density in urban areas can be extrapolated from the data presented in Table IV-6. The servic station density shown for four

77<

Table IV-6

SERVICE STATION DENSITY IN FOUR METROPOLITAN AQCRs

AQCR	Number of[*] Service Stations (1977)	AQCR[**] Population (1975)	Service Station[†] Density (number/1000 population)
Boston	2,353	4,039,800	0.6
Dallas	3,218	2,970,900	1.1
Denver	1,277	1,389,000	0.9
Los Angeles	7,298	14,072,400	0.5

Source:

[*] ADL

[**] U.S. Department of Commerce, Bureau of Economic Analysis, 1973.

[†] SRI estimates.

78<

metropolitan AQCRs is somewhat variable, with no apparent regional pattern evident. Based on these data, an average of 0.7 service station per 1000 population was estimated. This number can be applied generally to urban areas throughout the United States. Urbanized areas* provide the best population base. The 1970 population residing in urbanized areas was 118,447,000 (Bureau of the Census, 1975). Thus, service stations in urbanized areas are estimated at 83,000, or 45% of all stations.

An emission rate can be estimated as follows.

(1) 70.0×10^9 gallons of leaded gasoline are sold annually by service stations.

(2) The average number of gallons pumped per service station is 3.8×10^5 gal. (There are approximately 184,000 service stations in the United States.)

(3) Assume that all service stations have uniform pumping volumes and that three service stations are co-located in urban areas. Although there is great variability in both the pumping volume and the number of stations located in the same area, we believe that our assumptions provide a reasonable estimate considering the limited data available.

(4) The ethylene dibromide emission rate for three co-located service stations is:

(Number of Stations) (Volume of Gasoline Pumped) (Emission Factor) = Emission Rate;

that is, (3) (3.80×10^5 gal/yr) (0.00039 g/gal) = 4.45×10^2 g/yr = 1.41×10^{-5} g/s.

Monitoring data for ethylene dibromide were collected in the vicinity of service stations in three cities (Phoenix, Los Angeles, and Camden, New Jersey) by Midwest Research Institute (1976). There was no information given on the amount of leaded gasoline pumped. The ambient ethylene dibromide concentrations ranged from 10 to 60 ppt with sampling periods of from 12 to 18 hours. Los Angeles showed the lowest concentrations (averaging about 14 ppt), indicating that the vapor recovery system on gasoline pumps effectively reduces ethylene dibromide releases to the atmosphere.

---

*Defined by the Bureau of Census as the central city or cities and surrounding closely settled territories. All sparsely settled areas in large incorporated cities are excluded by this definition. Densely populated suburban areas, however, are included (U.S. Department of Commerce, Bureau of the Census, 1972 County and City Data Book).

79<

The most comprehensive data were collected in the vicinity of a heavily used intersection in Phoenix and were used as the basis for estimating a dispersion curve. Seven service stations were located in the sampling area. Measured ethylene dibromide concentrations ranged from 25 to 65 ppt. Figure IV-1 shows the variations in concentration within the sampling area. The samples were collected over an 18-hour period. The mean value within the 500 m radius was 48 ppt with a standard deviation of 10 ppt. The estimated concentration at 1 km is 30 ppt if no service stations are located outside the perimeter. The traffic passing through the intersection was reported to be 38,000 vehicles per day.

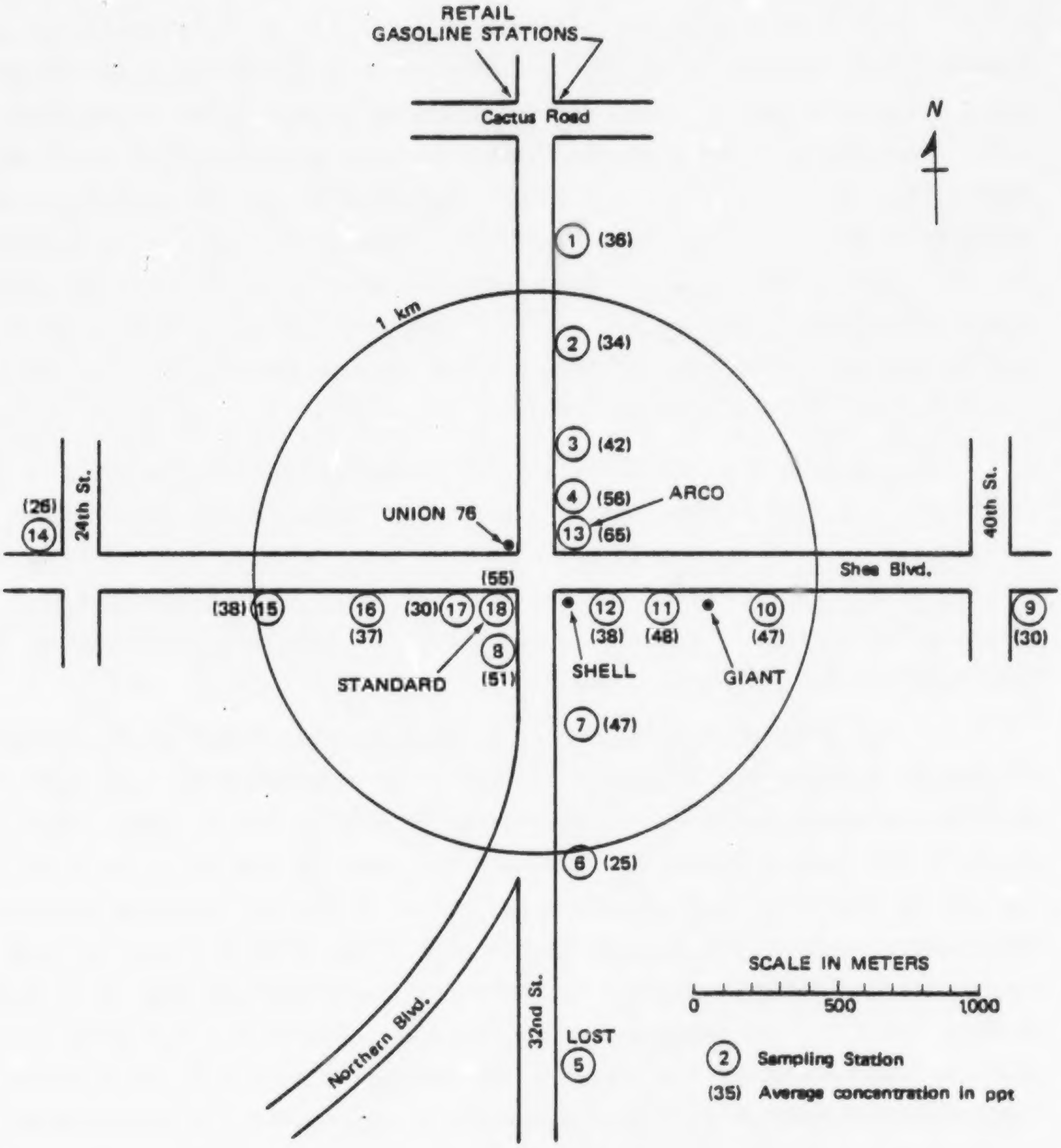
Assuming that 30 ppt at 1 km approximates the concentration representative of a 24-hour sampling period, an 8-hour worst-case concentration can be estimated at 40 ppt. Because that value is related to seven service stations, the corresponding value for three service stations is estimated as 17 ppt. The annual average exposure can then be estimated as 2.0 ppt (0.013 $\mu g/m^3$) at 1 km.

The dispersion modeling curve applied to exposures in the vicinity of service stations was extrapolated from rough dispersion modeling for an area source conducted by Youngblood of EPA (1977c) for benzene. The shape of the curve remains approximately the same for ethylene dibromide, but its relative position changes based on the difference in emission rates. The dispersion curve for an area source of 0.25 km^2 (500 m on a side) was considered to be representative of three co-located service stations. Mara and Lee (1977, p. 33) developed an equation by regression analysis to characterize this curve for benzene. By incorporating the emission rates for ethylene dibromide into that equation, a new equation is formulated, as follows:

$$C = (0.013)\ D^{-0.91} \qquad (4.1)$$

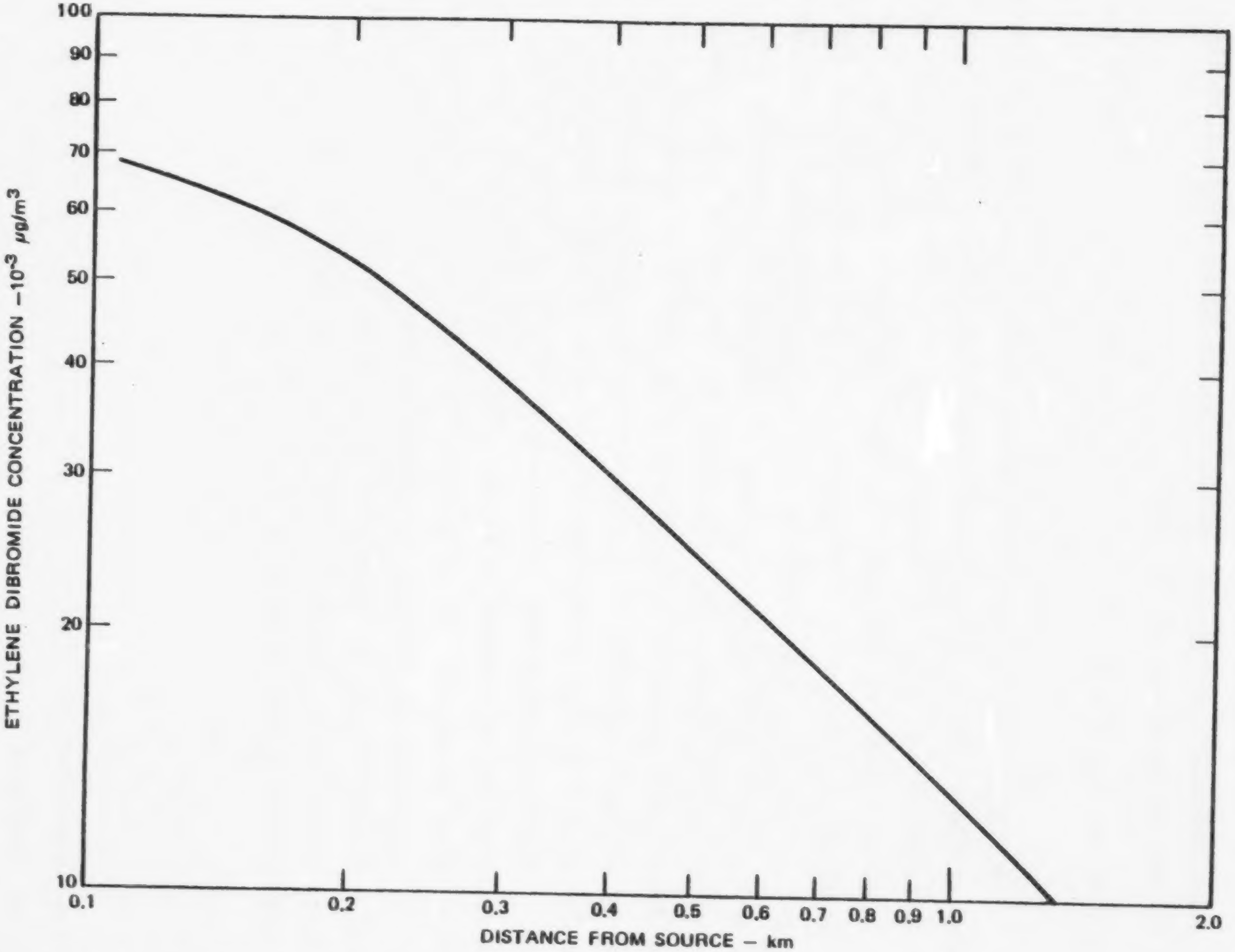
where C is the concentration at distance D, and 0.013 is the product of the emission rate and the system constant. The results of the calculations are shown in Figure IV-2. Note that concentrations can be expected to drop below 1 ppt just beyond 1 km from the source area.

80<


RETAIL
GASOLINE STATIONS
Cactus Road
N
1 (36)
1 km
2 (34)
3 (42)
4 (56)
ARCO
UNION 76
13 (65)
(26)
14
24th St.
40th St.
Shea Blvd.
(55)
(38) 15
16
(37)
(30) 17
18
8
(51)
STANDARD
12
(38)
11
(48)
10
(47)
SHELL
GIANT
9
(30)
7 (47)
6 (25)
SCALE IN METERS
0
500
1000
32nd St.
Northern Blvd.
LOST
5
2 Sampling Station
(35) Average concentration in ppt

Source: Midwest Research Institute, 1976

FIGURE IV-1. AVERAGE CONCENTRATION OF ETHYLENE DIBROMIDE IN AIR AT 18 SAMPLING STATIONS NEAR A RETAIL GASOLINE SITE IN PHOENIX, ARIZONA



Source: SRI estimates after Youngblood (1977c)

FIGURE IV-2. PROJECTED DISPERSION CURVE FOR ANNUAL AVERAGE CONCENTRATIONS IN THE VICINITY OF SERVICE STATIONS

The population exposed to annual average concentrations between 5.1 and 10.0 ppt is estimated as follows:

$$\text{Exposed Population} = \pi\ (0.3\ \text{km})^2\ (27{,}633)^{*}\ (1318\ \text{people/km}^2)$$
$$= 10{,}000{,}000$$

The population exposed to annual average concentrations between 1.0 and 5.0 ppt is estimated as follows:

$$\text{Exposed Population} = \pi\ [(1\ \text{km})^2 - (0.3\ \text{km})^2]\ (27{,}633)^{*}\ (1318\ \text{people/km}^2)$$
$$= 100{,}000{,}000$$

The summary results are presented in Table IV-7. It is recognized that these estimates are only rough approximations, based on assumptions of uniform distribution of three co-located service stations in urbanized areas, uniform pumping volume, and average population density. In reality, more service stations are located in commercial areas than in residential areas, and pumping volumes vary substantially. In addition, although it is likely that several service stations are located in the same general area, the average number is not known. If these areas are considered to be commercial, they may have either a higher than average population density within 1 km (because of a high percentage of apartments nearby), or one much lower than average (because of a high percentage of businesses and few residences of any kind). People residing near areas with more than three co-located service stations may be exposed to higher annual average benzene concentrations than those estimated. It is likely from this analysis that population exposed is overestimated, whereas the exposure levels themselves may be underestimated. Further study is warranted to determine a more accurate estimate of exposure levels based on pumping volumes, co-location of service stations, their distribution within an urban area, and emission rates.

---

[*] Number of locations of service stations within urbanized areas assuming three at each location.

83<

Table IV-7

SUMMARY OF POPULATION EXPOSED TO ETHYLENE DIBROMIDE FROM GASOLINE SERVICE STATIONS

EXPOSURE TYPE	EXPOSURE TIME	ANNUAL EXPOSURE	POPULATION EXPOSED TO EDB CONCENTRATIONS (ppt)*			
			1.0–5.0	5.1–10.0	260.0	TOTAL
SELF-SERVICE PUMPING	1.7 MIN.	1.5 HR.	–	–	30,000,000	30,000,000
RESIDING IN THE VICINITY	24 HR.	ANNUAL AVERAGE**	100,000,000	10,000,000	–	110,000,000

* To convert to $\mu g/m^3$, divide concentrations by 130.

** To convert annual average exposures to 8-hour worst case, multiply concentrations by 10.

Source: SRI estimates

84<

V PETROLEUM REFINERIES

A. Sources

Petroleum refineries are sources of atmospheric emissions of ethylene dibromide. Ethylene dibromide is a major ingredient in the antiknock "motor mix" blended into leaded gasoline at each refinery. Motor mix is manufactured at five locations (see Chapter III) and shipped in tank cars or trucks to petroleum refineries. It is then transferred to storage sites and used as needed. The average content of ethylene dibromide in antiknock mixes is 17.9% by weight.

A limited sampling study in the vicinity of two petroleum refineries was conducted by Midwest Research Institute (1976). The results are shown in Table V-1. Concentrations of ethylene dibromide ranged from 6 to 16 ppt within 3 km of the refinery at Ponca City, Oklahoma, and from 10 to 26 ppt within 2 km of the site at Paulsboro, New Jersey. MRI concluded that the source of all ethylene dibromide emissions was the gasoline bulk loading area. Although samples were collected in the vicinity of the tetraethyl lead storage, the mixing facility, the leaded gasoline storage area, and the gasoline pumping station, none of these samples suggested that those areas were the source of substantial emissions.

In light of the monitoring data, we decided to limit our analysis of petroleum refineries to an estimate of exposures related to bulk loading of leaded gasoline. The next section describes the methodology and the estimated population exposed to this source.

B. Methodology

The general methodology described in Chapter III was used as the basis for determining exposure levels from petroleum refineries. The dispersion of ethylene dibromide was approximated based on the rough dispersion model developed by Youngblood of EPA (1977b) for benzene.

Table V-1

MONITORING DATA IN THE VICINITY OF PETROLEUM REFINERIES

Refinery	Location	Average Sampling Time (hr)	Average EDB Concentration (ppt)*	Standard Deviation
Conoco	Ponca City, OK	18	8.8	2.4
Mobil	Paulsboro, NJ	18	15.5	5.0

---

*To convert to μg/m^3, divide by 130.

Source: Midwest Research Institute, 1976.

86<

Mara and Lee (1977) present a complete discussion of the model and its application to benzene emissions. A projected dispersion curve was developed for ethylene dibromide and applied to the largest refineries by computer program to estimate the exposed population.

To estimate the amount of leaded gasoline bulk loaded at each refinery, a number of assumptions were necessary:

(1) Gasoline production can be estimated at approximately 45% of crude capacity (Moore, personal communication, 1977).

(2) Approximately 75% of gasoline is transported by pipeline (Bureau of Mines, 1977); thus, 25% is bulk loaded.

(3) Approximately 80% of gasoline is leaded (Ethyl Corporation, 1976).

Appendix A presents the results of these calculations.

An emission factor was estimated for bulk loading of leaded gasoline at refineries based on earlier work conducted by PEDCo (1977) for benzene. They had estimated an emission factor for bulk loading of gasoline. That factor was extrapolated to approximate ethylene dibromide as follows:

$$\left(\begin{matrix}\text{Benzene Emission}\\ \text{Factor}\end{matrix}\right)\left(\frac{\text{Vapor Pressure EDB}}{\text{Vapor Pressure Benzene}}\right)\left(\frac{\text{Conc. EDB in Gasoline}}{\text{Conc. Benzene in Gasoline}}\right) = \text{EDB Emission Factor;}$$

that is,

$$(1.1 \times 10^{-4}\ \text{kg/m}^3)\ \left(\frac{12}{100}\right)\ \left(\frac{0.05}{2.0}\right) = 3.3 \times 10^{-7}\ \text{kg/m}^3.$$

If more than one refinery was located in a particular city, we assumed that the refineries were co-located, and we summed their emission rates. Although several cities have three or more refineries, it is also true that few people generally live near such complexes. Thus, with this method, the exposed population is minimized, whereas the exposure level is maximized for a particular city.

Locations having refineries with crude capacities exceeding 5 x 10^6m^3/yr were evaluated individually. The remainder was evaluated on a statewide basis. Appendix A lists the location of and the estimated gasoline production at each refinery.

Emission rates were estimated for each location based on the estimated volume of gasoline bulk-loaded and an 8-hour-a-day, 7-day week. Appendix A lists the estimated emission rates for each location or state.

The dispersion curve of ethylene dibromide from petroleum refineries was approximated from the curve representing ground-level point source emissions (curve A) developed by Youngblood for benzene (1977b). As described in Chapter III, the shape of the curve remains approximately the same for ethylene dibromide, but its relative position changes based on the difference in emission rates. Mara and Lee (1977, p. 24) developed an equation by regression analysis to characterize the curve for benzene. By incorporating the emission rates for ethylene dibromide and by adjusting to the available monitoring data, a new equation can be formulated.

Monitoring data from the Ponca City site were used because the refinery there represented an isolated location with few other ethylene dibromide sources. The estimated emission rate for the refinery (see Table A-1 in Appendix A) is 2.07×10^{-5} g/s. The average measured ethylene dibromide concentration at 2.5 km is approximately 0.08 $\mu g/m^3$ (10 ppt). Those data are then substituted into the general equation to determine the system constant (A) as follows:

$$C = A\ E_A D^{-1.48} \qquad (5.1)$$

where C is 8-hour worst-case concentration at distance D, and E_A is the emission rate for the particular refinery.

$$(0.08) = A\ (2.07 \times 10^{-5})\ (2.5)^{-1.48} \qquad (5.2)$$

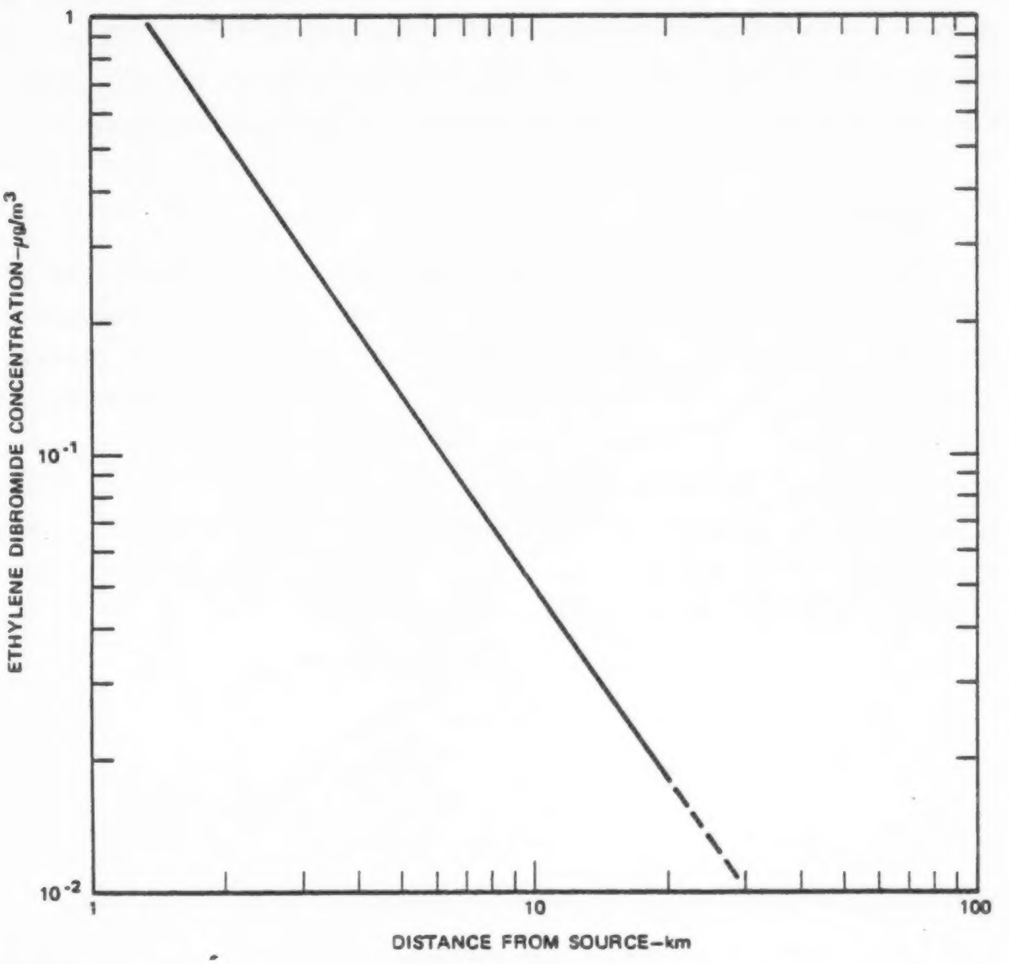
$$A = 1.5 \times 10^4 \qquad (5.3)$$

A is then extrapolated to annual average conditions by multiplying by 0.1. Equation (5.1) is then rearranged as follows:

$$D_i = (1.40 \times 10^2)\ \left(\frac{E_A}{C_i}\right)^{.6757} \qquad (5.4)$$

where C_i is the specified concentration (i.e., 1.0, 5.0, 10.0, and so on; input data, however, are in $\mu g/m^3$); and D_i is the distance at which the specified concentration is found. The projected dispersion curve for petroleum refineries based on an emission factor of 10×10^{-5} g/s is shown in Figure V-1.

88<



* Based on an emission rate of 10×10^{-5} g/s

Source: SRI estimates after Youngblood (1977b)

FIGURE V-1. PROJECTED DISPERSION CURVE* FOR PETROLEUM REFINERIES

89<

The computer program developed by SRI (Mara and Lee, 1977) was used to calculate the exposed population within ranges of concentrations at each location from Equation (5.4). A complete discussion of the program is found in Chapter III. Because the dispersion modeling results are unverified at distances greater than 20 km from the source location, the computer program automatically cut off calculations when a distance of 20 km was attained and calculated the concentration (C_i) at 20 km. Distances within 500 m of the point source were assumed to be within the plant perimeter and were not included in the estimate of exposed population.

C. Exposures

The population exposed to atmospheric ethylene dibromide from petroleum refineries by plant location and by state is shown in Appendix A. Table V-2 presents the summary results. More than 99% of the exposed population was found at locations having a total refining capacity exceeding 5 x $10^6 m^3$/yr. Of the more than 2 million people exposed to annual average ethylene dibromide concentrations greater than 1.0 ppt, 90% are estimated to be exposed to concentrations from 1.0 to 5.0 ppt. Approximately 0.1% are estimated to be exposed to ethylene dibromide levels exceeding 40.0 ppt (400.0 ppt 8-hour worst case).

Table V-2

ESTIMATED POPULATION EXPOSED TO ETHYLENE DIBROMIDE FROM PETROLEUM REFINERIES

	Annual Average[*] Ethylene Dibromide Concentrations (ppt)[†]					
	1.0-5.0	5.1-10.0	10.1-20.0	20.1-40.0	>40.0	Total
Exposed Population	2,000,000	170,000	53,000	16,000	3,000	2,200,000

---

[*] To convert to 8-hour worst case, multiply concentrations by 10.

[†] To convert to μg/m^3, divide by 130.

Source: SRI estimates.

91<

VI STORAGE AND DISTRIBUTION OF GASOLINE

A. Sources

Storage and distribution of gasoline represent potential sources of atmospheric ethylene dibromide in the environment. Ethylene dibromide can escape via two main emission pathways: (1) evaporation and spills during loading and unloading of gasoline at bulk terminals and (2) spills from collisions in transportation. Ethylene dibromide transfers normally occur at manufacturing and formulating facilities and were considered in Chapter III.

Gasoline transfers normally occur at petroleum refineries and at numerous storage sites throughout the United States. Gasoline is usually stored in closed containers in remote locations. Although loss from storage tanks through evaporation has been observed, most of the ethylene dibromide in the environment is believed to have been released during the loading and unloading of the gasoline. Spills from collisions involving gasoline transfer vehicles account for negligible losses of ethylene dibromide.

B. Methodology and Exposures

1. Storage

Storage facilities consist of closed storage vessels, including pressure, fixed-roof, floating-roof, and conservation tanks. Ordinary fixed-roof tanks store less volatile petroleum products, whereas floating-roof tanks are most commonly used to store gasoline. Emissions of ethylene dibromide from storage in a floating-roof tank occur primarily from standing and withdrawal (wetting) losses. Fixed-roof tanks have "breathing" losses caused by expansion and contraction of the vapors because of diurnal changes in atmospheric temperature. Because of the low volume of gasoline stored in fixed-roof tanks, breathing losses are not a significant source of ethylene dibromide.

Standing emissions are caused by improper fit of the seal and shoe to the vessel shell. Small losses also occur when vapor escapes between the flexible membrane seal and the roof. Withdrawal or wetting losses are caused by evaporation from the tank walls as the roof descends during emptying operations (PEDCo, 1977).

Emission factors of ethylene dibromide as a result of these losses were estimated by extrapolating from benzene emission factors developed by PEDCo (1977, p. 4-65) as follows:

Storage	Benzene Emission Factor (kg/m^3)*	Estimated EDB Emission Factor (kg/m^3)†
Gasoline		
Standing losses	3.3×10^{-5}	
Withdrawal losses	2.6×10^{-5}	
Total:	5.9×10^{-5}	1.77×10^{-7}

---

*PEDCo estimates (1977).

†SRI estimates based on differences in vapor pressure and concentration between benzene and ethylene dibromide. See Chapter II for a more detailed discussion.

Gasoline bulk storage terminals are generally near urban demand centers, commonly in highly industrialized areas or on the city periphery where population density is low.

Rough estimates of ambient ethylene dibromide concentrations for the vicinity of storage sites can be based on the emission factors, assumed storage volumes, and the results of the dispersion model discussed in Chapter III. An average gasoline storage terminal is assumed to have the following characteristics: average tank size, 8.7×10^3 m^3; 30-day retention time; 10 gasoline storage tanks of average size; facility size, 0.25 km^2. The emission rate is calculated as follows:

(emission factor) x (tank volume) x (number of tanks) = emission rate;

that is, $(1.77 \times 10^{-7}\ kg/m^3)\ (8.7 \times 10^3\ m^3/30\ days)(10) = 5.13 \times 10^{-4}\ kg/day$

$= 5.94 \times 10^{-6}\ g/s.$

93<

The ambient ethylene dibromide concentrations can be estimated by extrapolating from the dispersion modeling calculations of Youngblood (1977c) that assume uniform emissions througnout the terminal area. By applying the estimated emission rate to the dispersion modeling results presented in Table IV-4 (Mara and Lee, 1977) for the indicated terminal area of 0.25 km^2, the following estimate can be made:

8-hour Worst-Case Exposure Levels at 300 m

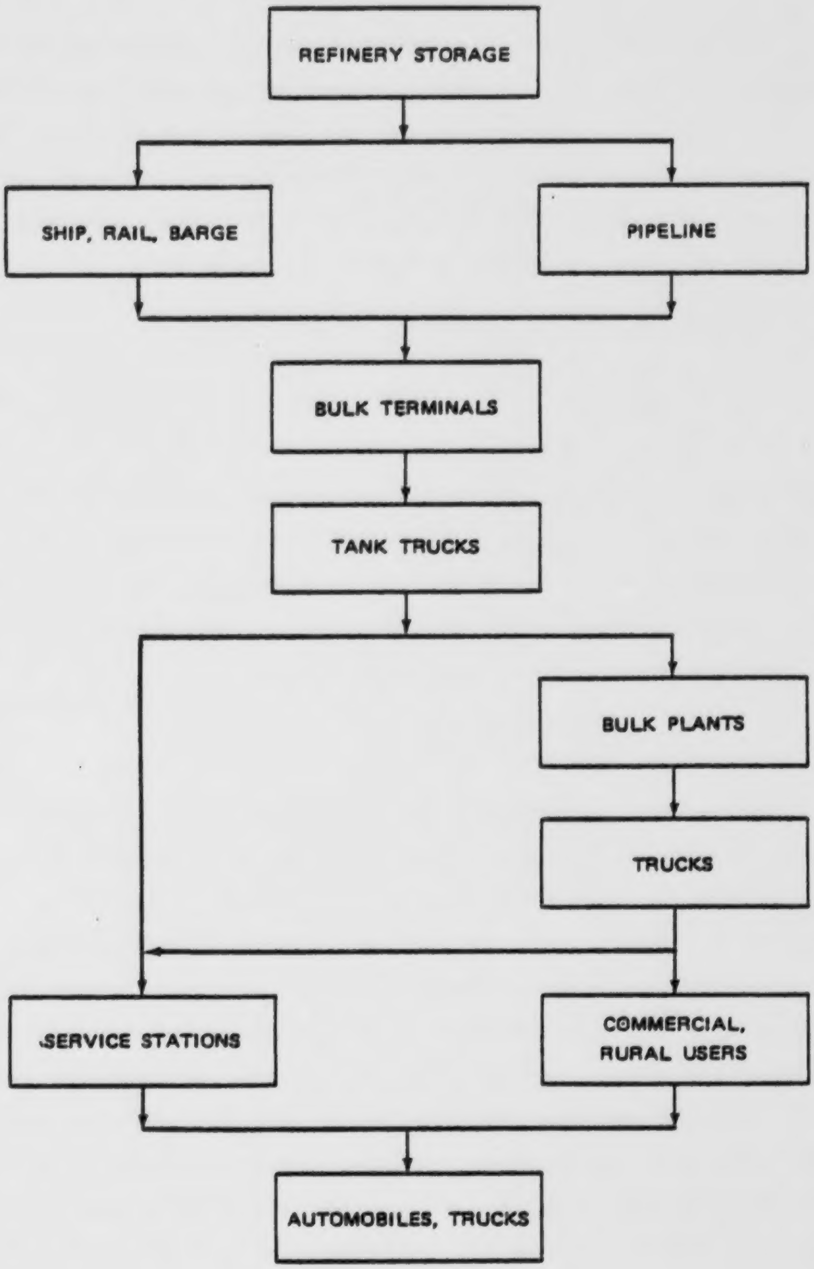
$$\begin{aligned}\left(\frac{5.94 \times 10^{-6}\ \text{g/s}}{100\ \text{g/s}}\right) (900\ \mu\text{g/m}^3) &= 5.35 \times 10^{-5}\ \mu\text{g/m}^3 \\ &= 6.95 \times 10^{-3}\ \text{ppt.}\end{aligned}$$

Therefore, annual average and 8-hour worst-case concentrations at 300 m of the site are well below the detection level of 1.0 ppt. From this analysis it appears that the number of people exposed to ambient ethylene dibromide concentrations above the detectable limit in the vicinity of gasoline storage terminals is negligible.

2. Distribution Systems

The gasoline distribution system involving transport from the petroleum refineries to the consumer may also be a source of atmospheric ethylene dibromide. The U.S. gasoline distribution system is illustrated in Figure VI-1. Bulk terminals represent intermediate stations set up to serve near-source regional markets. Gasoline at bulk terminals is transferred directly from the refinery by ships, rail tank cars, barges, and pipelines. Bulk plants, on the other hand, are designed for local markets and their supplies are distributed by tank trucks. Service stations that fuel privately owned motor vehicles are supplied by tank trucks from either bulk terminals or bulk plants. Privately owned commercial operations, such as those providing fuel for vehicles of a company fleet, are generally supplied by tank trucks from an intermediate bulk installation.

Most of the emissions take place during transfers of the gasoline to tanks and tank trucks. Such losses occur at a rate directly proportional to the amount of gasoline passing through the particular location. Because many tank trucks are filled at one bulk terminal or plant, ethylene dibromide emissions from that procedure are potentially much greater. As empty tank trucks are filled, hydrocarbons in the vapor space are displaced to the


REFINERY STORAGE
SHIP, RAIL, BARGE
PIPELINE
BULK TERMINALS
TANK TRUCKS
BULK PLANTS
TRUCKS
SERVICE STATIONS
COMMERCIAL, RURAL USERS
AUTOMOBILES, TRUCKS

SOURCE: PEDCo, 1977

FIGURE VI-1. THE GASOLINE MARKETING DISTRIBUTION SYSTEM IN THE UNITED STATES

95<

atmosphere unless vapor collection devices have been provided. The quantity of hydrocarbons contained in the displaced vapors depends upon the vapor pressure, temperature, method of tank filling, and conditions under which the truck was previously loaded. Figure VI-2 is a schematic drawing of liquid and vapor flow through a typical bulk terminal.

Gasoline is loaded from storage tanks to transport trucks (tank cars) by two basic methods: top loading and bottom loading (PEDCo, 1977). Top loading can be done by splash fill or submerged fill. The former method involves free fall of gasoline droplets and thus promotes evaporation and possibly liquid entrainment of those droplets in the expelled vapors. In subsurface or submerged filling, the gasoline is introduced below the surface of the tank. Bottom loading of gasoline is comparable to submerged top loading.

Vapor recovery systems are designed to reduce the overall hydrocarbon emission losses (including ethylene dibromide) for both loading and unloading. For bottom loading, the vapor recovery system may achieve 100% efficiency (PEDCo, 1977). Although it is difficult to quantify, vapor collection for top loading is generally not so efficient as that for bottom loading. An overall 95% efficiency of vapor recovery and containment can be assumed for both loading and unloading (PEDCo, 1977, p. 4-60).

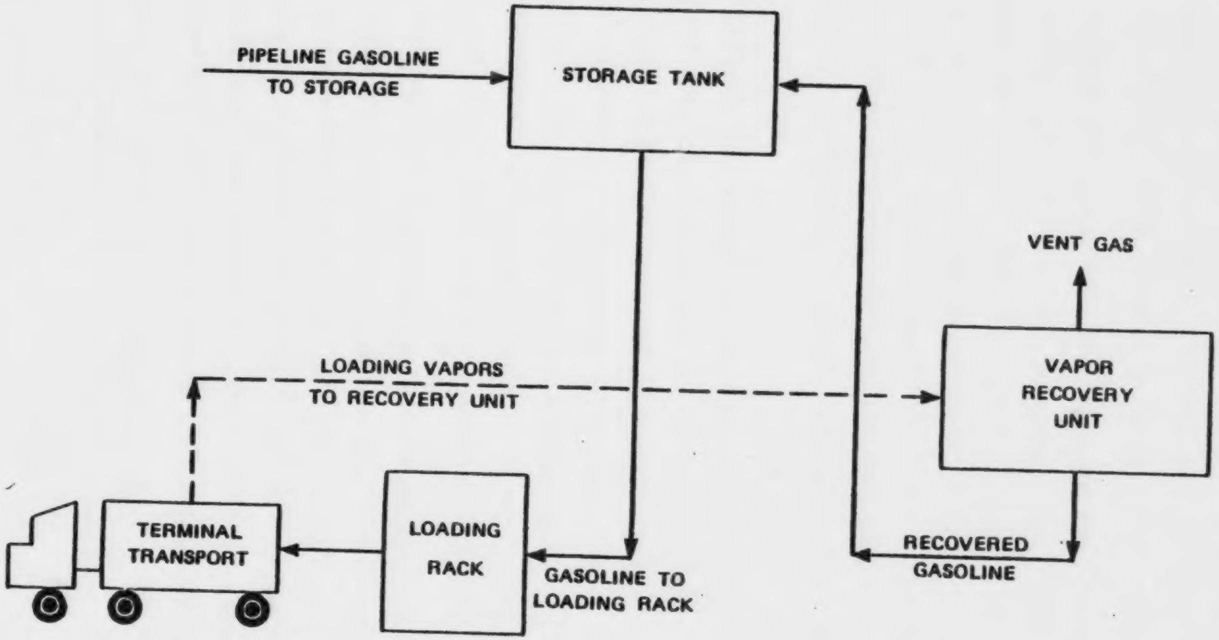
Rough estimates of ambient ethylene dibromide concentrations related to gasoline distribution can be based on emission factors, assumed transfer volumes, and the dispersion modeling results discussed in Chapter III. Emission factors related to the loading and unloading of gasoline were estimated for benzene by PEDCo (1977, p. 4-65), and have been extrapolated to estimate ethylene dibromide concentrations. The estimates follow:

Distribution	Benzene Emission Factor (kg/m^3)*	Estimated EDB Emission Factor (kg/m^3)†
Loading	1.1×10^{-4}	3.3×10^{-7}
Unloading	1.1×10^{-5}	3.3×10^{-8}

---

*PEDCo estimates (1977).

†SRI estimates based on differences in vapor pressure and concentration between benzene and ethylene dibromide. See Chapter II for a more detailed discussion.


PIPELINE GASOLINE TO STORAGE
STORAGE TANK
VENT GAS
LOADING VAPORS TO RECOVERY UNIT
VAPOR RECOVERY UNIT
TERMINAL TRANSPORT
LOADING RACK
GASOLINE TO LOADING RACK
RECOVERED GASOLINE

SOURCE: PEDCo, 1977

FIGURE VI-2. VAPOR AND LIQUID FLOW IN A TYPICAL BULK TERMINAL (Floating-Roof Tank)

97<

A gasoline bulk storage terminal of the same characteristics as described in the previous section is assumed. In addition, continuous loading and unloading operations are assumed over a five-day work week, eight hours a day. The emission rates are calculated as follows:

Loading

(Emission factor) x (Average Tank Size) x (# of Tanks) = Emission Rate

that is,

$$(3.3 \times 10^{-7}\ \text{kg/m3})\ (8.7 \times 10^{3}\ \text{m}^{3}/30\ \text{days})\ (10) = 9.57 \times 10^{-4}\ \text{kg/day}$$
$$= 3.32 \times 10^{-5}\ \text{g/s.}$$

Unloading

$$(3.3 \times 10^{-8}\ \text{kg/m}^{3})\ (8.7 \times 10^{3}\ \text{m}^{3}/30\ \text{days})\ (10) = 9.57 \times 10^{-5}\ \text{kg/day}$$
$$= 3.32 \times 10^{-6}\ \text{g/s.}$$
$$\text{Total emission rate} = 3.65 \times 10^{-5}\ \text{g/s.}$$

The ambient ethylene dibromide concentration can be estimated from the dispersion modeling calculation of Youngblood (1977b) by assuming ground-level point source emissions (Curve A). When the estimated emission rate is applied to the results presented in Table III-4 (Mara and Lee, 1977), the following estimate can be made:

8-Hour Worst-Case Exposure Levels at 300 m

$$\left(\frac{3.65 \times 10^{-5}\ \text{g/s}}{100\ \text{g/s}}\right)(14{,}000\ \mu\text{g/m}^{3}) = 5.11 \times 10^{-3}\ \mu\text{g/m}^{3}$$
$$= 0.7\ \text{ppt}$$

Approximate annual average concentration = 0.07 ppt.

From this analysis, it appears that concentrations at 300 m of the loading and unloading area are generally below 1.0 ppt. Concentrations may be higher in some cases if a large volume of gasoline (larger than the average value used in this analysis--$2.9 \times 10^{3}\ \text{m}^{3}$/day loaded and unloaded) is loaded and unloaded during one 8-hour period. Thus, although occupational exposures may be high, exposures to the general public appear to be minimal.

98<

VII URBAN EXPOSURES RELATED TO AUTOMOBILE EMISSIONS

A. Sources

Urban exposures to ethylene dibromide come from many sources, including gasoline evaporation, gasoline service stations, losses through transportation and storage of gasoline, and, in some cases, manufacturing and formulating facilities. However, ethylene dibromide is not routinely monitored in the ambient air, and few sampling data exist. Therefore, to determine average urban exposures, it is necessary to restrict the analysis to automobile emissions.

Although antiknock mixture for automobiles contains 17.9% by weight ethylene dibromide, antiknock mixture for aviation fuel contains 35.7% by weight. It was beyond the scope of this study to evaluate airports as a source of urban emissions. However, ambient ethylene dibromide concentrations in the vicinity of airports servicing a high percentage of piston-engine planes may be higher than ambient concentrations in the surrounding area.

As previously discussed, the ethylene dibromide content in leaded gasoline averages 0.05% and accounts for 80% of the gasoline sold. Tests by EPA's Mobile Source Air Pollution Control Laboratory in Ann Arbor, Michigan, have indicated that ethylene dibromide is destroyed in the combustion process, producing various bromines in the exhaust gases (Kittredge, personal communication, 1977). However, evaporation of ethylene dibromide on the carburetor and from the fuel tank does occur. The testing results for three categories of automobiles are shown in Table VII-1.

A few monitoring data have been collected in urban areas. An early study conducted by Midwest Research Institute (MRI) (1975) measured ethylene dibromide concentrations in four locations in three cities (Phoenix, Los Angeles, Seattle). As shown in Table VII-2, the concentrations ranged from 8.3 to 13.0 ppt (0.69 to 0.11 $\mu g/m^3$). In a second study,

Table VII-1

AUTOMOTIVE ETHYLENE DIBROMIDE EMISSION FACTORS (g/g lead/gal gasoline)

Vehicle Type	Low	High
Uncontrolled vehicle (pre-1972)	0.00144	0.00362
Pre-1978 controlled vehicle	0.00098	0.00250
Post-1978 controlled vehicle	0.00033	0.00085

Source: Kittredge, 1977

Table VII-2

MONITORING DATA FOR ETHYLENE DIBROMIDE IN URBAN AREAS

Location	Number of Sites	Average Sampling Time (hr)	Average EDB Concentration		Reference
			$\mu g/m^3$	ppt	
Phoenix	1	17	0.069	8	1
Los Angeles	1	16	0.110	13	1
Seattle	2	12	0.083	11	1
Phoenix	10	18	0.360	47	2
Los Angeles	9	18	0.124	16	2
Kansas City*	1	18	0.060	8	2

---

*Suburban area

1. Midwest Research Institute (1975)
2. Midwest Research Institute (1976)

MRI (1976) conducted much more extensive sampling near highly trafficked sites in Phoenix and Los Angeles. While the two Los Angeles average concentrations were very close, the Phoenix measurements differed by a factor of 5. No detailed meteorological information was available. An additional sampling site in a suburban area of Kansas City provided results very close to the Los Angeles measurements. Although no explanation was offered for the Phoenix samples, MRI concluded that the effect of heavily trafficked freeways on the ethylene dibromide levels in the two cities was not discernible. They further concluded that the ubiquitous nature of ethylene dibromide is probably the result of widely dispersed sources of emission in urban/industrial areas.

B. Methodology and Exposures

Only limited data are available concerning urban exposures from automobile emissions. Consequently, it is difficult to develop accurate techniques to predict ethylene dibromide levels in urban areas. Uncertainties include the ethylene dibromide content in gasoline, control technology, the deterioration of the control technology over time, and the dispersion characteristics of ethylene dibromide under variable meteorological conditions. A simplified model was employed to provide general estimates of ambient concentrations and of exposed population.

The emission factor is estimated from the information presented in Table VII-1. The average emission factor for an uncontrolled vehicle is 0.00253 g/g lead/gal. Assuming 2.5 g lead per gallon of leaded gasoline, the estimated emission factor is 0.0063 g/gal. This factor will provide a slightly high estimate of ambient ethylene dibromide levels because it assumes all automobiles using leaded gasoline have emissions comparable to pre-1972 models. In fact, the 1975 model year was the first in which automobiles were required to run on unleaded gasoline, but controls to reduce carburetor evaporation were introduced in the 1972 model year.

The Hanna-Gifford dispersion model (Gifford and Hanna, 1973) as applied by Schewe (1977) for benzene is used for this analysis and modified for ethylene dibromide. Mara and Lee (1977) contains a complete discussion of this model and its application to benzene. Because ethylene dibromide undergoes combustion, only evaporation is considered. The modified equation to estimate the emission rate for ethylene dibromide is as follows:

$$Q\ \text{evap} = (0.0063\ \text{g/gal})\left(\frac{\text{annual travel miles per vehicle}}{\text{average miles per gallon}}\right)(\#\ \text{veh. regis.})\left(\frac{1}{\text{area}}\right)$$

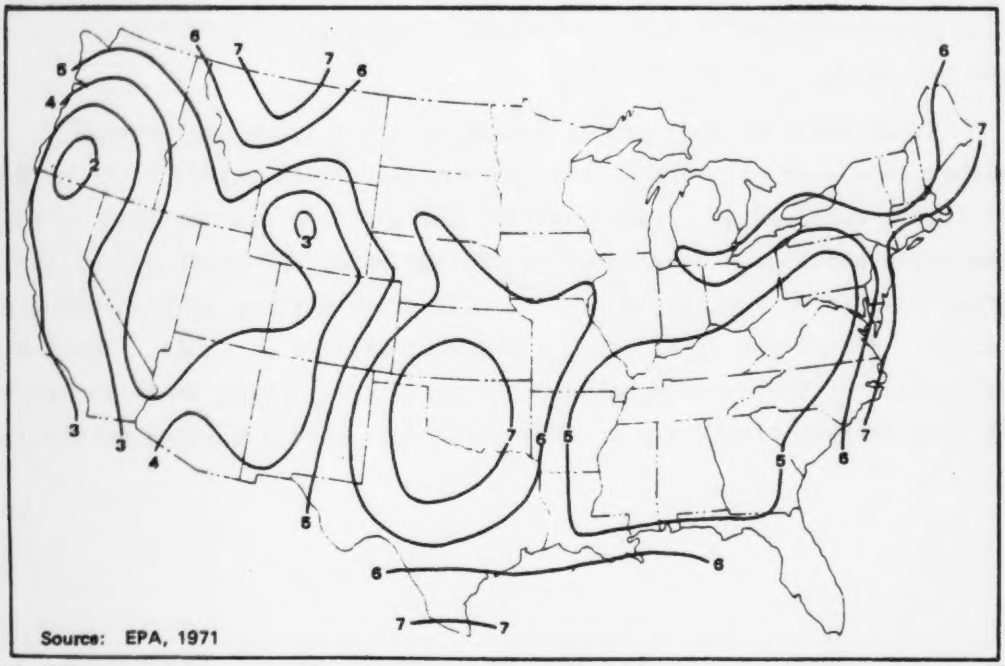
If 12,000 miles per year for each vehicle and 12 miles per gallon are assumed (Department of Transportation, 1974), the above equation becomes

$$Q\ \text{evap} = (2.0 \times 10^{-7}\ \text{g/s}) \times \left(\frac{\#\ \text{Veh. Regis.}}{\text{area}}\right)$$

To calculate the annual average areawide ethylene dibromide concentration, the following equation can be used:

$$\chi_A = \frac{225\ Q\ \text{evap}}{u}$$

where u is wind speed (m/sec). The average annual wind speed, u, in the area of study was obtained from Figure VII-1. Because wind speed (and thus dispersion) increases in the afternoon, the morning values were used to estimate higher concentrations. The number 225 is an empirical factor derived from several studies that gave very good results for long-term averages; it applies to light-duty vehicles such as passenger cars.



Source: EPA, 1971

FIGURE VII -1. ISOPLETHS (m/sec) OF MEAN ANNUAL WIND SPEED THROUGH THE MORNING MIXING LAYER

Because of the general unavailability of 1976 data for all urban areas, 1973 data were used as much as possible in this estimate. Comparisons of 1973 with 1976 data indicated that the change was less than 3% and had a negligible effect on the final results. The following data sources were used:

- 1973 Standard Metropolitan Statistical Area (SMSA) and county populations--U.S. Bureau of the Census, 1976, Series P-25, No. 618.
- 1973 SMSA and county automobile registrations--U.S. Department of Transportation, Federal Highway Administration, 1974, Table MV-21.
- Average annual wind speed--EPA, 1972, Publication No. AP-101.
- SMSA, county and city land areas--Bureau of the Census, 1972 County and City Data Book.

A detailed analysis was conducted for the six largest cities in the U.S. (populations of more than 1 million). Table VII-3 presents the results. Suburban areas are defined as those areas outside the central city but within the SMSA. Because no VMT and registration data were available at the city level, they were extrapolated either from SMSA data or county data and were based on the fraction of the population residing in each area. The results show that the annual average estimated ethylene dibromide concentrations in city and suburban areas range from 0.5 to 2.2 ppt and 0.1 to 1.0 ppt, respectively.

It is expected that people living in urban areas are exposed to higher levels of ethylene dibromide from automobile emissions than those living in rural areas. Consequently, our approach was designed to maximize the urban population considered in the analysis. Although 43% of the total urban population resides in central cities (as defined by the Bureau of the Census), 83% of the total urban population resides in SMSAs. Thus, a greater percentage of the urban population is captured by using SMSAs as study areas. The six largest cities are in SMSAs with more than 2 million population.

Table VII-3

ESTIMATES OF AVERAGE ANNUAL ETHYLENE DIBROMIDE CONCENTRATIONS FOR CITIES WITH POPULATIONS EXCEEDING 1,000,000

City	SMSA Population 10^3	City Population 10^3	City Area $10^9\,m^2$	Automobile Registration	Qt* 10^{-10} g/s-m^2	Wind Speed m/s	EDB Concentration			
							Central City		Suburban	
							$10^{-3}\mu g/m^3$	ppt	$10^{-3}\mu g/m^3$	ppt
Chicago	6,998.8	3,173	0.57	1,324,171	3.71	5	16	2.1	6.6	0.9
Detroit	4,446.3	1,387	0.35	675,065	3.08	6	11	1.4	7.7	1.0
Houston	2,163.4	1,320	1.1	701,766	1.01	6	4	0.5	0.74	0.1
Los Angeles	6,938.3	2,747	1.2	1,490,483	1.98	3	14	1.8	3.0	0.4
New York	9,746.4	7,647	0.77	1,707,891	3.54	7	11	1.4	1.8	0.2
Philadelphia	4,826.3	1,862	0.33	944,660	4.57	6	17	2.2	1.0	0.1

---

*Assume 80% of vehicles use leaded gasoline.

Source: SRI estimates based on Hanna-Gifford dispersion model as applied by Schewe (1977).

To analyze the remaining SMSAs, the following population size categories were employed (U.S. Bureau of the Census, 1976, Series P-25, No. 618):

SMSA Population Size Category	Number of Areas
2,000,000 or more	15
1,000,000 - 2,000,000	20
500,000 - 1,000,000	37
250,000 - 500,000	63
fewer than 250,000	124

SMSA composite ethylene dibromide concentrations were estimated for seven areas that represent four population size categories (see Table VII-4). All calculations gave ethylene dibromide concentrations below 1 ppt.

The estimates of urban exposures from automobile emissions are approximate estimates that are based on a simple dispersion model. In certain locations and under certain meteorological conditions, ethylene dibromide concentrations may be a factor of 10 higher than those listed. In addition, central city areas (as shown in Table VII-3) may have consistently higher levels than surrounding areas because of traffic density, frequency of intersections, and street density. Because the model only includes automobile emissions, areas with substantial commercial or bus transportation may have higher levels than estimated. Also, the model is extremely sensitive to area size, as Table VII-2 indicates. Thus, ethylene dibromide concentrations in the composite SMSA provide the most reasonable estimate of the average annual exposures for an urbanized area.

The total estimated urban population exposed to annual average ethylene dibromide in concentrations greater than 1.0 ppt from automobile emissions is shown in Table VII-5. The 1974 SMSA populations of Detroit and Chicago were summed along with the central city population of Los Angeles, New York, and Philadelphia to estimate the population exposed to average annual ethylene dibromide concentrations of 1.0 to 5.0 ppt. The results indicate that 24 million people, or 15% of the total SMSA population, are exposed to average annual ethylene dibromide concentrations greater than 1.0 ppt. The apparent differences between the monitoring data can be explained in several ways. Our estimates concern annual average

Table VII-4

ESTIMATES OF ANNUAL AVERAGE ETHYLENE DIBROMIDE CONCENTRATIONS FOR SELECTED SMSAs

SMSA	Population	Area ($10^9 m^2$)	Automobile Registration	Qt* 10^{-11} $g/s\text{-}m^2$	Wind Speed m/s	EDB Concentration $10^{-3} \mu g/m^3$	EDB Concentration ppt
SMSAs >2,000,000							
Pittsburg	2,333,600	7.8	2,358,600	4.8	5	2.1	0.3
San Francisco	3,135,900	6.2	688,300	1.8	3	1.4	0.2
SMSAs 1,000,000 - 2,000,000							
Columbus	1,055,900	6.2	567,803	1.7	5	0.66	0.09
Milwaukee	1,423,200	3.7	642,531	2.8	5	1.2	0.2
SMSAs 500,000 - 1,000,000							
Sacramento	851,300	8.7	439,803	0.80	3	0.60	0.08
Providence Warwick Pawtucket	854,400	2.4	869,100	5.8	7	1.9	0.2
SMSAs 250,000 - 500,000							
Wichita	375,600	6.2	221,715	0.57	7	0.18	0.02
Harrisburg	425,500	4.1	198,997	0.77	5	0.35	0.05

---

*Assume 80% of vehicles use leaded gasoline.

Source: SRI estimates using Hanna-Gifford dispersion model as applied by Schewe (1977).

ethylene dibromide exposures from gasoline evaporation from automobiles within an entire urban area. The monitoring data, on the other hand, were collected generally near highly trafficked areas with nearby gasoline stations; such areas are treated as a separate source in this report. Incomplete combustion is not considered in the model and may also contribute to higher ambient levels. Uncertainties in the data used for the model calculations and the limited nature of the monitoring data are additional reasons for the differences. Given the widespread nature of ethylene dibromide in the urban atmosphere, additional research is required to improve these estimates of exposure.

Table VII-5

URBAN POPULATION EXPOSURES RELATED TO AUTOMOTIVE EMISSIONS

Source	Population Exposed to Annual Average[*] EDB Concentration of 1.0 - 5.0 ppt[†]
Automobile Emissions	24,000,000

---

[*] To convert to 8-hour worst case, multiply by 10.

[†] To convert to μg/m^3, divide concentrations by 130.

Source: SRI estimates.

BIBLIOGRAPHY

Applied Urbanetics, Inc., "Market Share Study," FEA Contract No. CO-06-60435, 200 pp. (1976).

Arthur D. Little, Inc., "Self-Serve Market Shares in Four Metropolitan Areas," memo to Richard J. Johnson, EPA, from E. Quakenbush and P. E. Mawn, June (1977).

Battelle-Columbus Laboratories, letter to Richard J. Johnson (Office of Air Quality Planning and Standards, EPA, Research Triangle Park), from C. W. Townley, concerning "Results of Self-Service Exposure Samples," May (1977).

Brown, S. L., F. Y. Chan, J. L. Jones et al., "Research Program on Hazard Priority Ranking of Manufactured Chemicals, Phase II-Final Report, Chemicals 1-20," SRI International, Menlo Park, California, report to the National Science Foundation, April (1975).

Ethyl Corporation, "Yearly Report of Gasoline Sales by States," Houston, Texas (1976).

Gifford, F. A. and S. R. Hanna, "Technical Note: Monitoring Urban Air Pollution," in Atmospheric Environment, Pergammon Press, Vol. 7, pp. 131-136 (1973).

Hartle, Richard, Industrial Hygiene Section, memo to Dr. Jerry Chandler, Criteria Manager, National Institute for Occupational Safety and Health concerning "Ethylene Dibromide Environmental Air Samples Collected at Gasoline Service Stations," 4 October (1977).

Joiner, Ronald L., Manager Toxic Sciences Group, Center for Occupational and Environmental Safety and Health, SRI International, personal communication, October (1977).

Kirk, R. E., Encyclopedia of Chemical Technology, 2nd Edition, Vol. 3, John Wiley and Sons, Inc., New York, p. 771 (1968).

Kittredge, George D., Senior Technical Advisor for Mobile Air Source Air Pollution Control, Office of Air and Waste Management, U.S. Environmental Protection Agency, memo to files concerning "Up-to-Date Estimate of Automotive Emission Factors," 26 September (1977).

Mara, S. J. and S. S. Lee, "Human Exposures to Atmospheric Benzene," SRI International, Menlo Park, California, prepared for U.S. Environmental Protection Agency, Contract No. 68-01-4314, October (1977).

Midwest Research Institute, "Sampling and Analysis of Selected Toxic Substances, Task II-Ethylene Dibromide," EPA 560/6-75-001, U.S. Environmental Protection Agency (1975).

_______________, "Sampling and Analysis of Selected Toxic Substances, Task IV-Ethylene Dibromide," EPA 560/6-76-021, U.S. Environmental Protection Agency.

Mitre Corporation, "Air Pollution Assessment of Ethylene Dibromide," prepared for the U.S. Environmental Protection Agency, Contract No. 68-02-1495 (1976).

Moore, Michael A., Manager, Petroleum Refineries, Energy Center, SRI International, personal communication, October (1977).

PEDCo Environmental, "Atmospheric Benzene Emissions," prepared for U.S. Environmental Protection Agency, Research Triangle Park (1977).

Schewe, George J., Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, memos to Richard J. Johnson, Strategies and Air Standards Division, U.S. Environmental Protection Agency, concerning "Estimates of the Impact of Benzene from Automotive Sources," of June 20, August 9, August 12 (1977).

Stolpman, Paul, Office of Air and Waste Management, U.S. Environmental Protection Agency, personal communication, October (1977).

U.S. Department of Commerce, Bureau of the Census, "Population Estimates and Projections," Series P-25, No. 618, Washington, D.C. (1976).

_______________, *1972 County and City Data Book*, Washington, D.C. (1973).

_______________, *Statistical Abstract of the United States*, Washington, D.C. (1975).

U.S. Department of Commerce, Bureau of Economic Analysis, "Projections of Economic Activity for Air Quality Control Regulations," NTIS PB-259-870 (1973).

U.S. Department of Interior, Bureau of Mines, "Mineral Industries Surveys--Crude Petroleum, Petroleum Products and Natural Gas Liquids," Washington, D.C., May (1976).

U.S. Department of Transportation, Federal Highway Administration, "Annual Miles of Automobile Travel," in Nationwide Personal Transportation Study, Report No. 2, 32 p. (1972).

_______________, "Highway Statistics," Washington, D.C. (1974).

_______________, "Motor Vehicle Registrations by Standard Metropolitan Statistical Areas," Table MV-21 (1974).

U.S. Environmental Protection Agency, "Mixing Heights, Wind Speeds, and Potential for Urban Area Pollution Throughout the Contiguous United States," in Publ. No. AP-101, Office of Air Programs, Research Triangle Park (1972).

_______________, "Compilation of Air Pollution Emission Factors," 2nd Edition, Publ. No. AP-42, Research Triangle Park (1976).

Youngblood, Phillip L., Monitoring and Data Analysis Division, U.S. Environmental Protection Agency, concerning "Use of Dispersion Calculations in Determining Population Exposures to Benzene From Chemical Plants," September 20 (1977b).

_______________, memo to Richard J. Johnson, Strategies and Air Standards Division, U.S. Environmental Protection Agency, concerning "Population Exposures to Benzene from Petroleum Refineries and Large Coking Plants," September 21 (1977c).

APPENDIX A

CAPACITIES AND EXPOSED POPULATION BY PETROLEUM REFINERY AND STATE

Table A-1

POPULATION EXPOSURES FROM PETROLEUM REFINERIES WITH CRUDE CAPACITIES EXCEEDING 5.0 x $10^6 m^3/yr$

Location§	Crude* Capacity $10^6 m^3$	Gasoline† Bulk Loaded $10^6 m^3$	Emission† Rate $10^{-5} g/s$	Population Exposed† to EDB (ppt)‡				
				1.0-5.0	5.1-10.0	10.1-20.0	20.1-40.0	>40.0
California								
Bakersfield								
Chevron USA Inc	1.51							
Kern Co. Refinery Co.	0.92							
Lion Oil Co. (TOSCO)	2.21							
Mohawk Petroleum	1.28							
Road Oil Sales	0.09							
Sabre Refining Co.	0.20							
Sunland Refining Co.	0.81							
West Coast Oil Co.	0.87							
Total	7.89	0.71	2.24	21,131	1,647	645		
Benicia								
Exxon Co.	5.12	0.46	1.45	578	45			
Carson								
Atlantic-Richfield	10.16							
Fletcher Oil	1.11							
Total	11.27	1.01	3.18	52,301	4,076	1,598		
El Segundo								
Chevron USA Inc.	23.51	2.12	6.68	4,554	355	139	55	
Los Angeles								
Union Oil Co. - Calif.	6.27	0.56	1.76	34,468	2,686			
Martinez								
Lion Oil Co. (TOSCO)	7.31							
Shell Oil Co.	5.80							
Total	13.11	1.18	3.72	2,065	161	63		
Richmond								
Shell Oil Co.	21.20	1.91	6.02	69,854	5,751	2,254	883	
San Francisco								
Union Oil Co. - Calif.	6.44	0.58	1.83	244,090	19,024			
Santa Fe Springs								
Gulf Oil Co.	2.99							
Powerline Oil Co	2.56							
Total	5.55	0.50	1.58	649	51			

Table A-1 (Continued)

Location§	Crude* Capacity $10^6 m^3$	Gasoline† Bulk Loaded $10^6 m^3$	Emission† Rate $10^{-5} g/s$	Population Exposed† to EDB (ppt)‡				
				1.0-5.0	5.1-10.0	10.1-20.0	20.1-40.0	>40.0
California (continued)								
Torrance								
Mobil Oil Corp.	7.17	0.65	2.05	45,977	3,583			
Wilmington								
Champlin Petroleum Co.	1.78							
Shell Oil Co.	5.22							
Texaco Inc.	4.35							
Total	11.35	1.02	3.21	1,692	132	52		
Delaware								
Delaware City								
Getty Oil Co. Inc.	8.13	0.73	2.30	2,367	185			
Georgia								
Savannah								
Amoco Oil Co.	8.71	0.78	2.46	741	58	23		
Illinois								
Joliet								
Mobil Oil Corp.	10.45	0.94	2.96	54,874	4,277	1,676		
Lemont								
Union Oil Co. - Calif.	8.76	0.79	2.49	1,812	141	55		
Robinson								
Marathon Oil Co.	11.32	1.02	3.21	2,554	199	78		
Wood River								
Amoco Oil Co.	5.51							
Shell Oil Co.	16.43							
Total	21.94	1.97	6.21	6,230	486	190	75	
Indiana								
East Chicago								
Energy Coop. Inc.	7.31	0.66	2.08	27,199	2,120			
Whiting								
Amoco Oil Co.	21.19	1.91	6.02	4,422	345	135	53	

114<

Table A-1 (Continued)

Location§	Crude* Capacity $10^6 m^3$	Gasoline† Bulk Loaded $10^6 m^3$	Emission† Rate $10^{-5} g/s$	Population Exposed† to EDB (ppt)‡				
				1.0-5.0	5.1-10.0	10.1-20.0	20.1-40.0	>40.0
Kansas								
El Dorado								
Getty Oil Co.	4.57							
Pester Refining Co.	1.31							
Total	5.88	0.53	1.67	137	11			
Kansas City								
Phillips Petroleum Co.	5.22	0.47	1.48	17,172	1,338			
Phillipsburg								
CRA Inc.	15.32	1.38	4.35	500	39	15		
Kentucky								
Catlettsburg								
Ashland Petroleum Co.	7.88	0.71	2.24	653	51			
Louisiana								
Baton Rouge								
Exxon Co.	29.60	2.66	8.38	142,341	14,995	5,877	2,303	
Belle Chasse								
Gulf Oil Co., Alliance Refinery	11.40	1.03	3.24	1,075	84	33		
Convent								
Texaco	8.13	0.73	2.30	676	53			
Garyville								
Marathon Oil Co.	11.61	1.04	3.28	1,093	85	33		
Lake Charles								
Cities Service Oil Co.	15.56							
Continental Oil Co.	4.82							
Total	20.38	1.83	5.76	2,339	189	71	28	
Meraux								
Murphy Oil Co.	5.37	0.48	1.51	383	30			
Norco								
Shell Oil Co.	13.93	1.25	3.94	1,400	109	43		
Minnesota								
Rosemount								
Koch Refining Co.	7.39	0.67	2.11	357	28			

115<

Table A-1 (Continued)

Location§	Crude* Capacity $10^6 m^3$	Gasoline† Bulk Loaded $10^6 m^3$	Emission† Rate $10^{-5} g/s$	Population Exposed† to EDB (ppt)‡				
				1.0-5.0	5.1-10.0	10.1-20.0	20.1-40.0	>40.0
Mississippi								
Pascagoula								
Chevron USA Inc.	16.30	1.47	4.63	22,980	2,990			
Missouri								
Sugar Creek								
Amoco Oil Co.	6.21	0.56	1.76	398	31			
Montana								
Billings								
Continental Oil Co.	3.05							
Exxon Co.	2.61							
Total	5.66	0.51	1.61	21,121	1,646			
New Jersey								
Linden								
Exxon Co.	16.54	1.49	4.69	43,867	6,270	2,457		
Paulsboro								
Mobil Oil Corp.	5.69	0.51	1.61	4,908	383			
Perth Amboy								
Chevron USA Inc.	9.75	0.88	2.77	34,629	6,750	2,646		
Westville								
Texaco, Inc.	5.12	0.46	1.45	4,261	332			
Ohio								
Lima								
Standard Oil Co. - Ohio	9.75	0.88	2.77	47,356	3,755	1,472		
Toledo								
Gulf Oil Co.	2.92							
Standard Oil Co. - Ohio	6.96							
Sun Petroleum Prod. Co.	7.26							
Total	17.14	1.54	4.85	105,557	8,227	3,224	1,264	
Oklahoma								
Ponca City								
Continental Oil Co.	7.31	0.66	2.07	9,845	767	301		

Table A-1 (Continued)

Location§	Crude* Capacity $10^6 m^3$	Gasoline† Bulk Loaded $10^6 m^3$	Emission† Rate $10^{-5} g/s$	Population Exposed† to EDB (ppt)‡				
				1.0-5.0	5.1-10.0	10.1-20.0	20.1-40.0	>40.0
Oklahoma (continued)								
Tulsa								
Sun Petroleum Products Inc.	5.14	0.46	1.45	8,397	654			
Pennsylvania								
Marcus Hook								
B P Oil Corp.	9.34							
Sun Petroleum Products Co.	9.58							
Total	18.92	1.70	5.36	6,764	527	207	81	
Philadelphia								
Atlantic-Richfield Co.	10.74							
Gulf Oil Co.	11.85							
Total	22.59	2.03	6.39	492,642	38,396	15,048	5,897	
Texas								
Baytown								
Exxon Co.	22.60	2.03	6.41	37,288	4,390	1,721	674	
Beaumont								
Mobil Oil Corp.	18.86							
Union Oil - Calif.	6.96							
Total	25.82	2.32	7.32	64,166	5,001	1,960	768	495
Borger								
Phillips Petroleum Co.	5.80	0.52	1.64	241	19			
Corpus Christi								
Champlin Petroleum Corp.	7.26							
Coastal States Petrochem.	10.70							
Howell Corp.	1.23							
Quintana Refining Co.	1.36							
Saber Refining Co.	0.54							
Southwestern Ref. Co.	6.96							
Sun Petroleum Products Co.	3.31							
Total	31.36	2.82	8.88	103,118	8,037	3,150	1,234	796
Deer Park								
Shell Oil Co.	17.06	1.54	4.85	1,043	81	32	12	
Houston								
Atlantic-Richfield Co.	17.76							
Charter Int. Oil Co.	3.77							
Crown Central Petr. Co.	5.80							

Table A-1 (Concluded)

Location [§]	Crude[*] Capacity $10^6 m^3$	Gasoline[†] Bulk Loaded $10^6 m^3$	Emission[†] Rate $10^{-5} g/s$	Population Exposed[†] to EDB (ppt)[‡]				
				1.0-5.0	5.1-10.0	10.1-20.0	20.1-40.0	>40.0
Texas (continued)								
Houston (continued)								
Eddy Refining Co.	0.18							
Total	27.51	2.48	7.81	121,104	9,439	3,699	1,450	934
Port Arthur								
American Petrofina Inc.	6.38							
Gulf Oil Co.	18.11							
Texaco Inc.	23.56							
Total	48.05	4.32	13.61	46,105	8,376	3,283	1,287	829
Sweeney								
Phillips Petroleum Co.	6.04	0.54	1.71	255	20			
Texas City								
Amoco Oil Co.	20.20							
Marathon Oil Co.	3.83							
Texas City Refining Inc.	4.32							
Total	28.35	2.55	8.46	27,648	2,155	845	331	213
Washington								
Anacortes								
Shell Oil Co.	5.28							
Texaco Inc.	4.53							
Total	9.81	0.88	2.77	544	42	17		
Ferndale								
Atlantic-Richfield Co.	5.57							
Mobil Oil Corp.	4.15							
Total	9.72	0.87	2.76	541	42	17		
Wyoming								
Casper								
Amoco Oil Co.	2.56							
Little American Ref. Co.	1.42							
Texaco Inc.	1.22							
Total	5.14	0.46	1.45	15,706	1,224			
Total Exposed Population[**]				2,000,000	170,000	53,000	16,000	3,000

---

[*] Oil and Gas Journal, May 28, 1977.

[†] SRI estimates.

[‡] To convert to μg/m³, divide by 130.

[§] When more than one refinery is located in a city, it is assumed that they are co-located and emission levels are summed.

[**] Rounded to two significant figures.

118<

Table A-2

POPULATION EXPOSURES IN STATES HAVING REFINERIES WITH CRUDE CAPACITIES LESS THAN 5 x $10^6 m^3/y$

State	Number* of Locations	Total* Crude Capacity $10^6 m^3$	Total† Gasoline Bulk Loaded $10^6 m^3$	Total† Emission Rate $10^{-5} g/s$	Rate† Per Location $10^{-5} g/s$	Population Exposed to EDB Concentrations of 1.0 to 5.0 ppt: Population per Location	State Total
Alabama	3	2.86	0.26	0.81	0.27	32	66
Alaska	2	4.24	0.38	1.20	0.60	3	6
Arizona	1	0.23	0.02	0.06	0.06	0	-
Arkansas	4	3.51	0.32	1.01	0.25	16	64
California	11	13.75	1.24	3.91	0.36	88	968
Colorado	3	3.73	0.33	1.04	0.35	15	45
Florida	1	0.33	0.03	0.09	0.09	15	15
Georgia	1	0.28	0.03	0.09	0.09	0	-
Hawaii	2	5.74	0.52	1.64	0.82	268	536
Illinois	6	16.11	1.45	4.57	0.76	364	2184
Indiana	5	4.81	0.43	1.35	0.27	67	335
Kansas	7	13.71	1.23	3.87	0.55	31	217
Kentucky	3	1.66	0.15	0.47	0.16	0	-
Louisiana	12	17.83	1.60	5.04	0.42	68	816
Maryland	1	1.65	0.15	0.47	0.47	396	396
Michigan	6	8.71	0.78	2.46	0.41	125	750
Minnesota	2	5.19	0.47	1.48	0.74	151	300
Mississippi	4	2.81	0.25	0.79	0.20	15	60
Montana	5	3.42	0.31	0.88	0.18	0	-
Nebraska	1	0.29	0.03	0.09	0.09	0	-
New Hampshire	1	0.75	0.07	0.22	0.22	31	31
New Jersey	1	0.35	0.03	0.09	0.09	100	100

120<

Table A-2 (Concluded)

State	Number* of Locations	Total* Crude Capacity 10^6m	Total† Gasoline Bulk Loaded 10^6m	Total† Emission Rate 10^{-5}g/s	Rate† Per Location 10^{-5}g/s	Population Exposed to EDB Concentrations of 1.0 to 5.0 ppt: Population per Location	Population Exposed to EDB Concentrations of 1.0 to 5.0 ppt: State Total
New Mexico	7	6.92	0.62	1.95	0.28	4	28
New York	2	6.21	0.56	1.76	0.88	842	1684
North Dakota	3	3.40	0.31	0.98	0.33	6	18
Ohio	3	7.35	0.66	2.08	0.69	420	1260
Oklahoma	10	19.03	1.71	5.39	0.54	45	450
Oregon	1	0.81	0.07	0.22	0.22	0	-
Pennsylvania	7	5.20	0.47	1.48	0.21	85	595
Tennessee	1	2.55	0.23	0.72	0.72	172	172
Texas	25	30.63	2.76	8.69	0.35	30	750
Utah	5	9.18	0.83	2.61	0.52	14	70
Virginia	1	3.08	0.28	0.88	0.88	271	271
Washington	2	1.76	0.16	0.50	0.25	21	42
West Virginia	3	1.12	0.10	0.32	0.11	0	-
Wisconsin	1	2.64	0.24	0.76	0.76	151	151
Wyoming	8	5.82	0.52	1.64	0.21	2	16
Total Exposed Population‡							12,000

---

*Oil and Gas Journal, May 28, 1977.

†SRI estimates.

‡Rounded to two significant figures.

SRI International

ASSESSMENT OF HUMAN EXPOSURES TO ATMOSPHERIC ETHYLENE DICHLORIDE

Final Report

May 1979

By:

Benjamin E. Suta

Prepared for:

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

Task Officer: Jack K. Greer, Jr.
Project Officer: Joseph D. Cirvello

Contract No. 68-02-2835 Task 17
SRI Project CRU-6780

Center for Resource and Environmental Systems Studies
Report No. 82

NOTICE

This report has been provided to the U.S. Environmental Protection Agency (EPA) by SRI International, Menlo Park, California, in partial fulfillment of Contract 68-02-2835. The opinions, findings, and conclusions expressed herein are those of the authors and are not necessarily those of EPA. Mention of company or product names is not to be considered an endorsement by EPA.

CONTENTS

LIST OF TABLES v

ACKNOWLEDGEMENTS vii

I INTRODUCTION 1

II SUMMARY 2

III CHEMICAL AND PHYSICAL PROPERTIES OF EDC AND ITS ENVIRONMENTAL BEHAVIOR 8

- Introduction 8
- Physical Properties 8
- Chemical Properties 9
- Environmental Behavior 11

IV EDC PRODUCTION AND USES 14

- Production 14
- Uses 14
- EDC Producers and Users 17

V POPULATION EXPOSURES FROM EDC PRODUCTION 21

- General 21
- Sources of Emissions 21
- Emissions 21
- Atmospheric Concentrations 23
- Exposure Estimates 28

VI POPULATION EXPOSURES FROM PRODUCERS THAT USE EDC AS A FEEDSTOCK 34

- General 34
- Sources of Emissions 34
- Emissions 35
- Atmospheric Concentrations 35
- Exposure Estimates 35

VII POPULATION EXPOSURES FROM EDC IN AUTOMOBILE GASOLINE 40
  General 40
  Exposures from Self-Service Operations 41
  Exposures in the Vicinity of Service Stations 48
  Urban Exposures Related to Automobile Emissions 54
  Summary of Urban Exposures from Automobile Gasoline . . 59
VIII OTHER ATMOSPHERIC EXPOSURE ROUTES 60
  General 60
  Dispersive Uses 60
  Transportation 61
  Waste Disposal 64
BIBLIOGRAPHY 66

TABLES

II-1 Summary of Estimated Population Exposures to Atmospheric EDC from Specific Emissions Sources 4

II-2 Estimated Atmospheric Emissions of EDC for 1977 5

III-1 Physical Properties of EDC 10

IV-1 EDC Consumption 16

IV-2 EDC Producers and Major Consumers 18

IV-3 1977 EDC Production by Direct Chlorination and Oxychlorination 19

IV-4 1977 Use of EDC Production Capacities 20

V-1 EDC Oxychlorination Vent Emissions 22

V-2 Estimated Atmospheric Emissions from EDC Production Facilities 24

V-3 Atmospheric EDC Monitoring Data for Calvert City, Kentucky 25

V-4 Atmospheric EDC Monitoring Data for Lake Charles, Louisiana 26

V-5 Atmospheric EDC Monitoring Data for New Orleans, Louisiana 27

V-6 Estimated One-Hour Average Downwind Atmospheric Concentrations of EDC ($\mu g/m^3$) 29

V-7 Estimated Human Population Exposures to Atmospheric EDC Emitted by Producers 31

V-8 Comparison of EDC Monitoring and Modeling Atmospheric Concentrations (ppb) 34

VI-1 Estimated EDC Atmospheric Emissions (g/s) for Plants that Use EDC as a Feedstock 37

VI-2 Estimates of Population Exposures to Atmospheric EDC Emitted by Plants that Use EDC as a Feedstock in Various Products 39

VI-3 Estimates of Total Population Exposures to Atmospheric EDC Emitted by Plants that Use EDC as a Feedstock . . . 40

VII-1 Self-Service Operations 43

VII-2 Gasoline Market Share of Self-Service Stations in Four AQCRs, Spring 1977 44

VII-3 Gasoline Market Share of Self-Service Stations in Two Metropolitan Areas, 1976 46
VII-4 Sampling Data from Self-Service Gasoline Pumping 47
VII-5 Estimates of EDC Exposures from Self-Service Gasoline Pumping 49
VII-6 Service Station Density in Four Metropolitan AQCRs . . . 51
VII-7 Rough Dispersion Modeling Results for EDC Emissions for Gasoline Service Stations 54
VII-8 Automotive EDC Emission Factors 56
VII-9 Distribution of Cities by 1970 Population 58
VII-10 Estimated U.S. City Exposures to EDC from the Evaporation of Automobile Gasoline 59
VIII-1 Summary of Uncontrolled Emission Factor for the Transfer of Benzene 63
VIII-2 Estimated 1977 EDC Emissions as Solid Waste and to Water from EDC Production 65

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the cooperation and guidance given by several individuals of the U.S. Environmental Portection Agency, Office of Air Quality Planning and Standards. Ken Greer, Strategies and Air Standards Division, and Dr. George H. Wahl, Jr., EPA Consultant, provided direction throughout the study. David Mascone of the Emission Standards and Engineering Division gave valuable assistance in regard to control technology and emission factors and George Schewe of NOAA provided input on atmospheric dispersion modeling.

Mr. Casey Cogswell, SRI International, Chemical Industries Center, generously provided information and guidance concerning the manufacturing and uses of ethylene dichloride.

I INTRODUCTION

This report is one in a series that SRI International is providing for the U.S. Environmental Protection Agency (EPA) to estimate populations at risk to selected pollutants. Primarily, this study has sought to estimate the environmental exposure of the U.S. populaton to atmospheric ethylene dichloride (EDC) emissions. The principal atmospheric sources we consider in this report are facilities at which EDC is produced or used as a chemical intermediate and gasoline that contains EDC as a lead scavenger. Possible exposures from transportation of EDC, disposal of EDC wastes, and other minor uses are also described.

II SUMMARY

EDC is one of the highest volume chemicals used in the United States, with approximately 5 million metric tons (mt) synthesized during 1977. More than 80% of the EDC produced is used in the synthesis of vinyl chloride monomer (VCM). The majority of the remaining production is used in the synthesis of 1,1,1-trichloroethane (1,1,1-TCE or methyl chloroform), trichloroethylene (TCE), perchloroethylene (PCE), vinylidine chloride (VDCM), and ethyleneamines (EA); EDC is also employed directly as a lead scavenger for gasoline.

EDC is a colorless, oily liquid that has a sweet taste, a chloroform-like odor, and a volatility similar to that of gasoline. It boils at $83.5^{\circ}C$, melts at $-35.4^{\circ}C$, and has a specific gravity of 1.2. It is relatively stable in water, but evaporates rapidly from water to the atmosphere where it is destroyed by photooxidation. Estimates of EDC's half-life in the atmosphere range from weeks to months, a period sufficiently long for aerial transport to play a major role in its distribution but relatively short for it to accumulate in the terrestrial and aquatic environment. It has a potential for bioaccumulation; however, no firm evidence now exists to support bioaccumulation in the marine environment or in other biota.

EDC does not occur naturally in the environment. Environmental exposures occur mainly from EDC lost during production, from EDC used as a chemical intermediate in producing other chemicals, or in its use in gasoline as a lead scavenger. Minor environmental exposures may occur through dispersive uses of EDC such as in grain fumigants, paints, coatings, adhesives, cleaning, and in the preparation of polysulfide compounds. Additional environmental exposures may occur from spills and venting during EDC transportation and from evaporation resulting from waste disposal.

Monitoring data for occupational exposures to EDC have been reported in the literature for more than four decades; however, the environmental monitoring data that have been collected date only from around 1975 and they are limited. A number of environmental monitoring studies have failed to find atmospheric EDC in the general U.S. environmental at the ppt detection level (Grimsrud and Rasmussen, 1975; Singh et al., 1977; and Hanst, 1978). PEDCo (1978) found EDC at the ppb level in the atmosphere surrounding three EDC production facilities. (The maximum integrated 24-hr value was 180 ppb.) Pellizzari (1978) reported the detection of EDC concentrations of less than 55 ppb near a chemical disposal site in New Jersey.

The current Occupational Safety and Health Administration (OSHA) standard for occupational exposure to EDC is 50 ppm (8-hr time-weighted average). In March 1976, the National Institute of Occupational Safety and Health recommended an exposure limit of 5 ppm (time-weighted averge for a 10-hr workday or less, a 40-hr workweek). These levels, however, were designed to protect against toxic effects other than cancer and may not provide adequate protection from potential carcinogenic effects (NIOSH, 1978).

Human population exposures to atmospheric EDC have been estimated for emissions resulting from its production, its use as a feedstock in the production of other chemicals, and its use as a lead scavenger in automobile gasoline. Other potential exposure routes such as emissions resulting from transportation and emissions from other product uses have also been described. The population exposure estimates given in Table II-1 are based on the calculated atmospheric emissions given in Table II-2.

These emission and exposure estimates have necessitated reliance on very limited data. Because of the paucity of measured atmospheric EDC data, it was necessary to approximate concentrations through the use of dispersion modeling. Moreover, the resulting estimates are subject to considerable uncertainty in regard to: (1) the quantity of EDC emissions, (2) EDC production and consumption levels, (3) certain source

Table II-1

SUMMARY OF ESTIMATED POPULATION EXPOSURES TO ATMOSPHERIC EDC FROM SPECIFIC EMISSIONS SOURCES

Annual Average EDC Concentration (ppb)[a]	Production Facilities[b]								Gasoline Service Stations[c]	Automobile Emissions[d]	Automobile Refueling[e]
	EDC	VCM	1,1,1-TCE	TCE	PCE	EA	VDCM	Lead Scavenger			
10	1,700										
6.00-10.00	3,300										
3.00- 5.99	28,000										
1.00- 2.99	280,000										(g)
0.60- 0.99	400,000	1,300									
0.30- 0.59	1,500,000	360				70					
0.10- 0.29	4,300,000[f]	30,000	1,700	390	80	17,000	270	1,900			
0.060-0.099	1,900,000[f]	42,000	16,000	10,000	500	8,000	3,400	3,400			
0.030-0.059	3,500,000[f]	260,000	83,000	47,000	17,000	43,000	34,000	25,000			
0.010-0.029	550,000[f]	940,000	170,000	140,000	250,000	37,000	90,000	350,000	1,000,000	13,000,000	
Total	12,500,000	1,300,000	260,000	200,000	270,000	110,000	130,000	380,000	1,000,000	13,000,000	30,000,000

---

[a] To convert to $\mu g/m^3$, multiply each exposure level by 4.1.

[b] Production facilities that either produce EDC or use EDC as a feedstock in the production of another chemical.

[c] These are exposures to people who reside near gasoline service stations.

[d] These are exposures from evaporative emissions from pre-1975 automobiles.

[e] These are exposures to people while refueling their automobiles at self-service gasoline stations.

[f] These are underestimates because the dispersion modeling results were not extrapolated beyond 30 km from each EDC production facility. There are additional people who are exposed to EDC concentrations of 0.01-0.1 ppb at distances greater than 30 km from the larger producton facilities.

[g] Estimated as 30 million people exposed to an EDC concentration of 1.5 ppb for 2.2 hr/yr. The annual average time-weighted exposure is 0.0004 ppb.

Table II-2

ESTIMATED ATMOSPHERIC EMISSONS OF EDC FOR 1977

	Emissions (1,000 mt/yr)
EDC production	
Fugitive	5.2
Storage	14.5
Direct chlorination	6.3
Oxychlorination	17.9
Subtotal	43.9
Production using EDC as Feedstock	
VCM	1.1
1,1,1-TCE	0.4
TCE	0.2
PCE	0.3
EA	0.3
VDCM	0.2
Lead scavenger	0.2
Subtotal	2.5
Automobile gasoline	
Service stations	0.1
Auto emissions	1.2
Subtotal	1.3
Other	
Dispersive uses	5.0
Transporation[a]	-.-
Waste disposal[a]	-.-
Total	52.7

---

[a] Not included. Rough order estimates place these emissions as much less than 2,400 mt/yr for transportation and much less than 29,100 mt/yr for waste disposal.

locations, (4) control technologies employed, (5) deterioration in control technologies over time, (6) physical characteristics of EDC sources, (e.g., stack height), (7) details on atmospheric dispersion and degradation, and (8) living patterns of the exposed population. Given these complex and variable factors, the accuracy of the estimates could not be assessed. Nevertheless, the estimates are believed to be a reasonable approximation of actual conditions. Comparisons of atmospheric monitoring and modeling data for EDC concentrations near 3 sites used in this report shows agreement within 70% and averaging 25%.

During 1977, 18 facilities produced an estimated 5 million mt of EDC. It is estimated that approximately 12.5 million people are exposed to average annual EDC concentrations of 0.01 to more than 10 ppb from this production. Estimates of exposures to concentrations of less than 0.1 ppb from production facilities are underestimates because the dispersion modeling results were not extrapolated beyond 30 km from the plants. There are additional people who are expected to be exposed to EDC concentrations of 0.01-0.1 ppb at distances of greater than 30 km from the larger production facilities. However, it is generally assumed that disperions modeling results are unreliable beyond 20 to 30 km from the source.

Estimates are given for exposures to EDC used as a feedstock in the production of VCM, 1,1,1-TCE, TCE, PCE, EA, VDCM, and gasoline lead scavengers. Many of these chemicals are produced at the same facilities that produce the EDC feedstock. Of the 28 producton plants involved, 18 also produce EDC. In 1977, approximately 5 million mt of EDC was required, with more than 80% used in producing VCM. More than 2 million people are exposed to annual average EDC concentratons of 0.01 to 1.0 ppb from these operations.

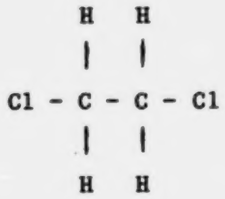
Leaded gasoline additives contain EDC as a lead scavenger. Although the EDC is expected to be destroyed during combustion, evaporative emissions occur during refueling operations and from the gas tanks and carburetors of automobiles. These emissions are expected to decrease as newer model automobiles replace the pre-1975 models. It has been estimated that approximately 30 million people are exposed to EDC concentrations of 1.5 ppb for 2.2 hr/yr while refueling their automobiles at self-service stations. Similarly, approximately 1 million people residing near gasoline service stations are exposed to average annual EDC concentrations of 0.01 to 0.03 ppb from refueling losses. Another 13 million are exposed to annual average EDC concentrations of 0.01 to 0.03 ppb from automobile evaporative emissions.

III CHEMICAL AND PHYSICAL PROPERTIES OF EDC AND ITS ENVIRONMENTAL BEHAVIOR*

Introduction

The Chemical Abstracts Service registry number of EDC is 000107062; the NIOSH number is KO05250. To minimize confusion between EDC ($C_2H_4Cl_2$) and cis and trans dichloroethylene ($C_2H_2Cl_2$), Drury and Hammons (1978) recommend that EDC be referred to as 1,2-dichlorethane in place of ethylene dichloride. Many synonyms and trade names are also used: Brocide; Destrucol Borer-Sol; Di-chlor-mulsion; sym-dichloroethane; alpha, beta-dichloroethane; dichloroethylene; Dutch liquid; EDC; ENT 1,656; ethane dichloride; ethylene chloride; glycol dichloride; and oil of the Dutch chemists (NOISH, 1977; Mitten et al., 1970).

The composition and structure of 1,2-dichloroethane (EDC) are indicated by the molecular formula, $C_2H_4CL_2$, and the line diagram,



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ Cl & - & C & - & C & - & Cl \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Physical Properties

EDC is a colorless, oily liquid that has a sweet taste and a chloroform-like odor (Hawley, 1977). It is volatile and evaporates at a rate 0.788 time that of carbon tetrachloride or gasoline (Whitney,

---

*The discussion given here has been summarized from a draft report by Drury and Hammons (1978).

1961). Air saturated with EDC contains 350 g/m^3 at 20°C and 537g/m^3 at 30°C. EDC is completely miscible with ethanol, chloroform, ethyl ether, and octanol (Windholtz, 1976; Johns, 1976). The partition coefficient, log P, of EDC between octanol and water is 1.48 (Radding et al., 1977), reflecting preferential solubility in organic media.

Vaporized EDC solvent is readily ignited--the closed cup flash point being only 13°C. The liquid is also flammable, burning with a smoky flame, but the ignition temperature is high, 413°C. Under a pressure of 1 atm, EDC steam distills at 71.9°C. The binary azeotrope contains 19.5% water; 14 other binary azeotropes are known (Mitten et al, 1970). A ternary azeotrope containing 78% 1,2-dichloroethane, 17% ethanol, and 5% water boils at 66.7°C. Other properties are given in Table III-1.

Chemical Properties

EDC is stable at ambient temperatures but slowly decomposes in the presence of air, moisture, and light. During decomposition the liquid EDC becomes darker in color and progressively acidic. It can corrode iron or steel containers, but these deleterious reactions are completely inhibited by small concentrations of alkyl amines (Hardie, 1964).

Both chlorine atoms in EDC are reactive and can be replaced by other substituents. This bifunctional nature of EDC makes it useful in the manufacture of condenstion polymers (Rothon, 1972). Hydrolysis of EDC, with slightly acidic 160°C to 175°C water at 15 atm, or with 140°C to 250°C aqueous alkali at 40 atm, yields ethylene glycol; at 120°C, the addition of ammonia under pressure to EDC yields ethylenediamine. 1,1,2-TCE and other higher chloroethanes are fomred by chlorinating EDC at 50°C in light from a mercury vapor lamp. EDC reacts with sodium polysulfide to form polyethylene tetrasulfide, and with oleum to give 2-chloroethylsulfuryl chloride. With Friedel-Crafts catalysis, both chlorine atoms in EDC can be replaced with aromatic ring compound (Hardie, 1964).

Table III-1

PHYSICAL PROPERTIES OF EDC

Molecular weight	98.96
Density, g/ml at 20°C	1.2351
Melting point, °C	-35.36
Boiling point, °C	83.47
Index of refraction, 20°C	1.4448
Vapor pressure, torr, at °C	
-44.5	1
-13.6	10
10.0	40
29.4	100
64.0	400
82.4	760
Solubility in water, ppm w/w at °C	
20	8,690
30	9,200
Biochemical oxygen demand (5 days), %	0
Theoretical oxygen demand, mg/mg	0.97
Measured chemical oxygen demand, mg/mg	1.025
Vapor density (air = 1)	3.42
Flash point, open cup, °C	13.0
Ignition temperature, °C	413.0
Explosive limit, % volume in air	
Lower	6.2
Upper	15.9
Specific resistivity	9.0×10^6
Viscosity, cP, at 20°C	0.840
Dielectric constant,ϵ	10.45
Surface tension, dyne/cm	33.23
Coefficient of cubical expansion, 10°C-30°C	0.0016
Latent heat of fusion, cal/g	21.12
Latent heat of vaporization, cal/g, at boiling point	77.3
Specific heat, cal/g °C	
Liquid at 20°C	0.308
Vapor, 1 atm at 97.1°C	0.255
Critical temperature, °C	288
Critical pressure, atm	53
Critical density, g/cm^3	0.44
Thermal conductivity, Btu/hr-ft^2 at 20°C	0.825
Heat of combustion, cP, kcal/g-mole	296.36
Dipole moment, ESU	1.57×10^{-18}
Conversion factors, 25°C, 760 torr	1 mg/L* = 1 g/m^3 = 247 ppm 1 ppm = 4.05 gm/m^3 = 4.05 g/L

Source: Draft report by Drury and Hammons (1978).

137<

Environmental Behavior

Bioaccumulation and Biomagnification

EDC's physical and chemical properties exhibit opposing tendencies with respect to bioaccumulation, but high vapor pressure and low latent heat of vaporization argue that the compound is exhaled from the lungs in the same condition in which it was inhaled. In fact, no firm evidence exists for the bioaccumulation of EDC in food chains under environmental conditions (Radding et al., 1977). Pearson and McConnell (1975) in searching for simple aliphatic chlorocarbons in several trophic levels of the marine environment near the industrialized area of Liverpool, found no evidence of EDC. In laboratory studies on oysters and fish using EDC labeled with carbon -14, Pearson and McConnell did see rapid storage of the chlorinated hydrocarbon up to an asymptotic level, but this accumulation was followed by loss of EDC on transfer of the organisms to clean sea water. Parallel analyses by chromatographic techniques showed reduced levels of EDC in the organisms, indicating that metabolism of the compound occurred in the tissues of both fish and oysters.

Biological Degradation

The conclusions of the few literature references to microbial degradation of simple chlorinated hydrocarbon compounds conflict. Some authors report these compounds are not metabolized either by aerobic or anaerobic microorganisms (Pearson and McConnell, 1975). Other microbiologists believe biodegradation can occur via co-metabolic processes (Horvath, 1972), but no evidence supporting biodegradation of EDC has been found. There is general agreement, however, that mammals metabolize these compounds, producing chlorinated acetic acids either directly or via chloroethanols. All of the resulting chlorinated acetic acids are susceptible to further degradation by microorganisms in sea water (McConnell et al., 1975).

Chemical Degradation

Photooxidative reactions involving atmospheric EDC probably result in monochloroacetyl chloride, hydrogen chloride, and monochloroacetic acid (Spense and Hanst, 1978). Alcohols, ketones, alkyl nitrates, and cleavage produces arising from intermediate alkoxy radicals are also possible products. Preliminary data indicate the half-life of EDC in the atmosphere may be about 3 to 4 months (Pearson and McConnell, 1975; EPA, 1975). Based on an average HO radical concentration of 0.8 x 10^{-14}M, Radding et al. (1977) estimated a combined oxidativephotolysis half-life of 234 hr. The recent calculations of Altshuller and the re- cent experiments of Snelson et al. (1978) indicate tropospheric life- times of EDC of approximately 0.75 to 1 year. Although the half-life remains to be determined definitively, available estimates make it clear that the lifetime of EDC in the troposphere, although short in an abso- lute sense, is sufficiently long for aerial transport to play a major role in its distribution.

EDC is resistant to hydrolysis. Radding et al. (1977) estimated a hydrolysis half-life of approximately 50,000 yr. This estimte is much longer than the 6- to 18-month half-lives observed for similar, but not identical, compounds subjected to a combination of hydrolysis, oxidation, and photolysis (Dilling et al., 1975); nevertheless, it appears that hydrolysis of EDC is slow compared to other pertinent environmental processes, such as volatilization or photolysis.

Dilling et al. (1975) and McConnell et al. (1975) studied the removal of compounds similar to EDC from water by adsorption on several common substrates. Dilling et al. observed little or no adsorption of chlorinated hydrocarbons on clay, limestone, sand, and peat moss in laboratory experiemtns that involved aqueous solutions containing 1 ppm organic contaminant. McConnell et al. reached similar conclusions about adsorption of chlorinated hydrocarbons from seawater by coarse gravels, but they found relatively high adsorption by Liverpool Bay sediments rich in organic detritus. The divergent conclusions of these studies probably reflect different experiemtnal conditions: The hydrocarbon concentrations in the experiments of Dilling et al. were well below the solubility limits of the various compounds used, and adsorption under these conditions is less likely than in Liverpool Bay, which receives large volumes of industrial and domestic effluents.

The relatively high vapor pressure of EDC causes rapid volatilization of the hydrocarbon from aqueous effluents. After 96 min at ambient temperature, about 90% of the EDC initially present in water at a concentration of 1 ppm evaporated (Dilling et al., 1975). this rate corresponds to a vaporization half-life of 29 min. Comparison of these data with those for other environmental removal processes indicate that volatilization is the chief process for removal of EDC from water.

Persistence

EDC has a long hydrolysis half-life, a short vaporization half-life from water, and a relatively short photooxidative half-life in the atmosphere. It is unlikely to accumulate in the environment. Note, however, that one of EDC's photooxidative products is chloroacetyl chloride, which may be sufficiently stable to reach the stratosphere and interact destructively with the ozone layer.

Environmental Transport

Because the vapor pressure of EDC is moderately high, most emissions from manufacturing operations occur as vapors that are vented directly to the atmosphere. Even when initially present in wastewater or solid waste products, EDC tends to transfer rapidly to the atmosphere. This volatility, coupled with an atmospheric half-life sufficiently long for aerial transport, results in most distribution of EDC in the environment occurring by aerial transport (McConnell et al., 1975; Pearson and McConnell, 1975). Some transfer of EDC from air to water also occurs, particularly as a result of rainfall. This effect is assumed to be minor when compared to aerial transport, but quantitative data comparing these transport routes are lacking.

IV EDC PRODUCTION AND USES

Production

The annual EDC production capacity for U.S. plants is approximately 7.3 million mt. From 1973 to 1977 the industry operated at about 60-70% of capacity, producing 4.6, 4.7, 3.7, 5.0, and 5.2 million mt, respectively. The overall production during these years may have been even higher than indicated because captive production is not always adequately recorded in published data. Future growth of the market is expected to average 4% to 5%/yr through 1981, at which time the demand for EDC is expected to be 6.6 million mt. Five of the major producing companies are currently expanding production facilities or are planning increased production in the near future (Chemical Marketing Reporter, 1977).

Uses

EDC is used primarily as a raw material in the synthesis of other chemicals, in particular for VCM, 1,1,1-TCE, TCE, PCE, VDCM, EA, and as a lead scavenger for gasoline. Primary uses of these compounds are as follows:

VCM	Its major use is in the production of PVC and its copolymer resins. Small amounts are used in polyvinylidene chloride and other copolymers.
1,1,1-TCE	Its major use is for solvent cleaning. Minor uses include aerosol propellant, solvent in adhesives and coating formulations, drain cleaner, and fabric spotting fluid.
TCE	It is almost entirely used as a metal-cleaning solvent.

PCE	Its major uses are for metal cleaning and dry cleaning.
EA	Its major uses are as a chelating agent and carbamate fungicide. Other uses include detergents and softening agents, specialty resins, epoxy hardeners, and corrosion inhibitors.
VDCM	It is used mainly in the production of polyvinylidene copolymers
Lead Scavenger	It is used in gasoline antiknock mixtures.

The quantities of EDC consumed for these and other uses are shown in Table IV-1. More than 80% of the EDC produced is used in the manufacture of VCM. Each of the other compounds listed above requires 2% to 3% of the total EDC produced. Exports account for about 3.4% of the EDC produced, and other minor products require less than 0.2% of EDC production.

Auerback Associates (1978) estimated EDC consumption for other minor uses in 1977 at about 5,000 mt. Of this subtotal, about 28% was used in the manufacture of paints, coatings, and adhesives. Extracting oil from seeds, treating animal fats, and processing pharmaceutical products required 23% of the subtotal. An additional 19% was consumed in cleaning textile products and polyvinyl chloride manufacturing equipment. Nearly 11% was used in the preparation of polysulfide compounds. Grain fumigation required about 10%. The remaining 9% was used as a carrier for amines in leaching copper ores, in the manufacture of color film, as a diluent for pesticides and herbicides, and for other miscellaneous purposes.

EDC Producers and Users

Table IV-2 lists the major EDC producers and consumers along with their estimated January 1979 installed production capacity. As the

Table IV-1

EDC CONSUMPTION
(Thousands of metric tons per year)

	YEAR					
Use	1973	1974	1975	1976	1977	1982[a]
VCM	3,645	3,871	3,015	4,079	4,300	5,635-6,140
1,1,1-TCE	184	198	155	213	215	260-280
TCE	141	121	92	99	83	85-110
PCE	104	98	89	89	87	87-95
EA	128	132	123	132	136	113-119
VDCM	83	92	83	88	97	125-135
Lead scavenger	106	97	80	93	89	39
Other	b	b	b	b	b	b
Net exports	167	(133)	(26)	(199)	177	180
Total	4,558	4,742	3,663	4,992	5,194	6,524-7,098

Source: SRI estimate.

[a] Projected consumption.

[b] Other uses, which are not included in consumption, in 1974 were estimated at 7,000 mt and at 5,000 mt in 1977.

table indicates, most EDC producers have the capacity to use most of the EDC they produce as feedstock for other products within their own plants. In fact, in recent years only a small fraction (10% to 15%) of the total production of EDC has been sold on the open market (US. International Trade Commission, 1973-1977).

EDC is produced by the "balanced process." This process involves a combination of direct chlorination of ethylene and oxychlorination of ethylene using hydrogen chloride, which in turn is produced in the cracking of EDC to VCM. The EDC manufactured by oxychlorination of ethylene is generally used captively as an intermediate in VCM production. Table IV-3 shows the percentages of EDC produced by direct chlorination and by oxychlorination, by producer.

Chemical producers rarely operate at maximum production capacity for a specific chemical. Table IV-4 shows the percentage of production capacity employed in 1977 to produce EDC and the major chemicals in which it is used as a feedstock.

Table IV-2

EDC PRODUCERS AND MAJOR CONSUMERS

(January 1, 1979, production capacities in thousands of metric tons)

Producer	Location	Capacity	VCM	1,1,1-TCE	TCE	PCE	EA	VDCM	Scavenger
Borden Chemical	Geismar, LA		224						
Conoco Chemical	Lake Charles, LA	524	525						
Diamond Shamrock	Deer Park, TX	145			17	45			
Diamond Shamrock	La Porte, TX	719	749						
Dow Chemical	Freeport, TX	726	150	167	51	0^b	60	45^c	
Dow Chemical	Oyster Creek, TX	499	525			0^b			
Dow Chemical	Pittsburg, CA					0^b			
Dow Chemical	Plaquemine, LA	953	936	112				45^c	
duPont	Antioch, CA								20^c
duPont	Corpus Christi, TX				0^b				
duPont	Deepwater, NJ								20^c
Ethyl Corp.	Baton Rouge, LA	318	248		15	14		20^c	
Ethyl Corp.	Houston, TX	118							20^c
B. F. Goodrich	Calvert City, KY	454	749						
Houston Chemical	Beaumont, TX								15^c
ICI America[a]	Baton Rouge, LA	318	224						
Monochem	Geismar, LA		0^b						
Nalco Chemical	Freeport, TX								5^c
PPG Industries	Lake Charles, TX	544	229	130	68	54		30^c	
PPG Industries	Guayanilla, PR	379	375						
Shell Chemical	Deer Park, TX	635	629						
Shell Chemical	Norco, LA	544	525						
Stauffer Chemical	Carson, CA	154	130						
Stauffer Chemical	Louisville KY					0^b			
Union Carbide	Taft, LA	68					70		
Union Carbide	Texas City, TX	68					60		
Vulcan Chemical	Geismar, LA	150		0^b		41			
Vulcan Chemical	Wichita, KS					0^b			
	Total	7,316	6,218	409	151	154	190	120	100

Source: SRI estimates.

[a] Plant was purchased from Allied Chemical in September 1978.
[b] Process does not use EDC as a feedstock.
[c] Rough order estimates.

Table IV-3

1977 EDC PRODUCTION BY DIRECT CHLORINATION AND OXYCHLORINATION

Producers	Locations	Direct Chlorination (%)	Oxychlorination (%)
Conoco Chemical	Lake Charles, LA	49.2	50.8
Diamond Shamrock	Deer Park, TX	35.8	64.2
Dow Chemical	Freeport, TX	57.1	42.9
Dow Chemical	Oyster Creek, TX	(b)	(b)
Dow Chemical	Plaquemine, LA	51.7	48.3
Ethyl Corporation	Baton Rouge, LA	52.7	47.3
Ethyl Corporation	Houston, TX	100.0	0.0
B. F. Goodrich	Calvert City, KY	33.3	66.7
ICI America[a]	Baton Rouge, LA	66.7	33.3
PPG Industries	Lake Charles, LA	77.2	22.8
PPG Industries	Guayanilla, PR	(b)	(b)
Shell Chemical	Deer Park, TX	66.2	33.8
Shell Chemical	Norco, LA	(b)	(b)
Stauffer Chemical	Long Beach, CA	69.2	30.8
Union Carbide	Taft, LA	100.0	0.0
Union Carbide	Texas City, TX	100.0	0.0
Vulcan Chemical	Geismar, LA	0.0	100.0

Source: Draft report by Drury and Hammons (1978).

[a] Plant was purchased from Allied Chemical in September 1978.

[b] Not available.

146<

Table IV-4

1977 USE OF EDC PRODUCTION CAPACITIES
(Thousands of metric tons)

Product	EDC Capacity[a]	EDC used in 1977 Production[b]	Percent Capacity Used
EDC	7,316	5,194	71.0
VCM	6,218	4,300	69.2
1,1,1-TCE	409	215	52.6
TCE	151	93	61.6
PCE	154	87	56.5
EA	190	136	71.6
VDCM	120	97	80.8
Lead scavenger	100	89	89.0

---

[a] See Table IV-2. This is the amount that would be used annually if the product was produced at 100% of capacity.

[b] See Table IV-1.

V POPULATION EXPOSURES FROM EDC PRODUCTION

General

As was shown in Table IV-2, most of the EDC produced is used as feedstock in the production of other chemicals, particularly VCM. the majority of both the EDC produced and the chemicals that use EDC as feedstock are made at the same facilities. thus, people residing near these production facilities can be exposed to atmospheric EDC from several types of production. Section VI sets forth the exposure from chemical production facilities that use EDC as a feedstock.

Sources of Emission

EDC producers and their individual capacities are listed in Table IV-2. The total annual capacity of the 18 plants listed is 7.3 million mt. Table IV-4 indicates that approximately 71% of the production capacity was used during 1977. Because production data for each plant are unavailable, we have assumed that each operates at 71% of capacity.

Emissions

Four principal sources of emissions have been identified: direct chlorination vent stack, oxychlorination vent stack, fugitive emissions, and emissions from tank storage.

As part of the Synthetic Organic Chemical Manufacturing Industry study under way in EPA's Emission Standards and Engineering Division of the Office of Air Quality Planning and Standards and as a result of the detailed study of the VCM industry, a significant amount of engineering data on the EDC industry are available. Table V-1 summarizes the data collected for oxychlorination vent emissions for 10 production plants. We applied the averge vent emission factor of those plants (1.0%) to plants for which no emission data are available. We estimated an emission factor of 0.22% for the direct chlorination process vent emissions, with fugitive emissions estimated at 0.1% of plant

Table V-1

EDC OXYCHLORINATION VENT EMISSIONS

Plant and Location	Oxychlorination Production[a] (g/s)	EDC Emissions[b] (g/s)	Emission Factor (g emission/ g production)
Conoco, Lake Charles, LA	5,987	12.3	0.0021
Diamond, Deer Park, TX	2,871	2.7	0.0009
Ethyl, Baton Rouge, LA	3,392	43.6	0.0129
Goodrich, Calvert City, KY	6,819	26.4	0.0039
ICI America, Baton Rouge, LA	2,366	70.1	0.0296
PPG, Lake Charles, LA	2,800	0.0	0.0000
Shell, Deer Park, TX	4,464	25.2	0.0056
Stauffer, Long Beach, CA	1,071	19.6[c]	0.0183
Vulcan, Geismar, LA	3,408	81.6[c]	0.0239
Dow, Oyster Creek, TX	5,609	0.0	0.0000
		Average	0.0097

---

[a] Total capacity given in Table IV-2 times 71% use times percent oxychlorination production given in Table IV-3.

[b] Source: EPA (1978).

[c] Based on an EPA engineering estimate.

production. Emissions for storage tanks at production facilities were estimated as 2.8 g/yr/kg of annual capacity (Mascone, 1978). Table V-2 gives the estimated emissions resulting from emission factors. Total EDC atmospheric emissions are estimated as 43.9 thousand mt/yr (1,312 g/s) or about 0.8% of the amount produced. The storage and direct chlorination emission rates are for uncontrolled plants. The industry now has some controls on these two emission points but data are insufficient to estimate the present degree of control.

Atmospheric Concentrations

Atmospheric monitoring data have been collected from three locations that have EDC production facilities (PEDCo, 1978). These three locations are (1) near the B. F. Goodrich plant in Calvert City, Kentucky, (2) near the Conoco plant in Lake Charles, Louisiana, and (3) near the Shell plant at Norco, Louisiana and the Union Carbine plant at Taft, Louisiana. The Goodrich, Conoco, and Shell plants each have annual EDC production capacities of approximately 500,000 mt. The Union Carbide plant has an annual capacity of approximately 70,000 mt.

Twelve monitoring stations were positioned around each location. Data were recorded for 10 days in New Orleans, 12 days in Lake Charles, and 13 days in Calvert City. The preliminary results of the monitoring data are summarized in Tables V-3 through V-5. Average 12- to 13-day atmospheric concentrations ranged from 0 to 5 ppb for the Calvert City stations, 1 to 43 ppb for the Lake Charles stations, and 0.1 to 12.1 ppb for the New Orleans stations. Individual 24-hr concentrations were much higher. Generally, the concentrations for locations near the plants in the Lake Charles area were almost 10 times those for the Calvert City and New Orleans areas. The differences may be attributable to meteorological conditions, plant production at sampling times, emission controls, positioning of the monitoring stations with respect to plant location and wind direction, or other EDC sources in the areas.

The monitoring data show that elevated EDC concentrations exist in the vicinity of at least 3 EDC production facilities; however, the data

Table V-2

ESTIMATED ATMOSPHERIC EMISSIONS FROM EDC PRODUCTION FACTILITIES

Plant	Location	Production[a]		Emissions (g/s)				
		10^3 mt/yr	(g/s)	Fugitive	Storage	Direct	Oxychlorination	Total
Conoco	Lake Charles, LA	372	11.800	11.8	33.0	12.8	12.6	70.2
Diamond	Deer Park TX	103	3,265	3.3	9.1	2.6	1.9	16.9
Diamond	La Porte, TX	510	16,190	16.2	45.3	17.8	15.8	95.1
Dow	Freeport, TX	515	16,345	16.3	45.7	20.5	67.3	149.8
Dow	Oyster Creek, TX	354	11,235	11.2	31.4	12.4	0.0	55.0
Dow	Plaquemine, LA	678	21,455	21.5	60.1	24.4	99.5	205.5
Ethyl	Baton Rouge, LA	226	7,160	7.2	20.1	8.3	43.7	79.3
Ethyl	Houston, TX	84	2,660	2.7	7.5	5.9	0.0	16.1
Goodrich	Calvert City, KY	322	10,220	10.2	28.6	7.5	26.6	72.9
ICI America	Baton Rouge, LA	226	7,160	7.2	20.1	10.5	70.6	108.4
PPG	Lake Charles, LA	386	12,250	12.3	34.3	20.8	0.0	67.4
PPG	Guayanilla, PR	269	8,533	8.5	23.9	9.4	41.4	83.2
Shell	Deer Park, TX	451	14,295	14.3	40.0	20.8	27.1	102.2
Shell	Norco, LA	386	12,250	12.3	34.3	13.5	59.4	119.5
Stauffer	Carson, CA	109	3,470	3.5	9.7	5.3	19.6	38.1
Union Carbide	Taft, LA	48	1,530	1.5	4.3	3.4	0.0	9.2
Union Carbide	Texas City, TX	48	1,530	1.5	4.3	3.4	0.0	9.2
Vulcan	Geismar, LA	107	3,380	3.4	9.5	0.0	80.8	93.7
	Total	5,194	—	164.9	461.2	199.3	566.3	1,391.7

Source: SRI estimates.

[a] Assumed to be 71% of production capacity.

Table V-3

ATMOSPHERIC EDC MONITORING DATA[a] FOR CALVERT CITY, KENTUCKY

Site No.	Relation to Goodrich Plant	Average (ppb)	Average (µg/m^3)	Range[b] (µg/m^3)
1	0.8 km SE	2.0	8.0	0.0 - 37.7
2	1.8 km SW	2.3	9.3	0.0 - 72.2
3	1.7 km SSW	0.1	0.5	0.0 - 4.1
4	2.0 km SSE	0.7	2.8	0.0 - 18.0
5	3.3 km SE	0.2	0.6	0.0 - 3.2
6	2.9 km E	0.0	0.1	0.0 - 0.5
7	2.5 km ENE	1.2	4.8	0.0 - 36.3
8	3.4 km NE	1.5	6.2	0.0 - 22.4
9	2.3 km NE	5.1	20.6	0.0 - 67.8
10	2.8 km N	3.6	14.6	0.0 - 59.9
11	2.3 km NNW	2.3	9.4	0.0 - 55.0
12	3.0 km NW	0.6	2.3	0.0 - 28.7

Source: Based on draft data supplied by PEDCo (1978).

[a] Observations are for thirteen 24-hr periods between August 27, 1978, and September 18, 1978.

[b] When duplicate quality control samples were taken at one site, the average of the two samples has been used.

Table V-4

ATMOSPHERIC EDC MONITORING DATA[a] FOR LAKE CHARLES, LOUISIANA

Site No.	Relation to Conoco Plant	Average (ppb)	Average ($\mu g/m^3$)	Range[b] ($\mu g/m^3$)
1	1.0 km S	26.4	106.7	1.4 - 269.5
2	0.7 km WNW	61.3	248.3	6.0 - 651.7
3	1.2 km WNW	5.0	20.2	0.0 - 67.2
4	0.7 km W	35.4	143.4	1.8 - 744.8
5	0.9 km SW	40.2	162.7	0.5 - 383.3
6	1.3 km WSW	11.2	45.4	0.0 - 171.6
7	3.0 km NW	1.1	4.5	0.0 - 27.3
8	2.8 km NNW	1.0	4.0	0.0 - 32.8
9	2.0 km NNW	1.6	6.5	0.0 - 30.2
10	1.5 km NNW	1.7	6.7	0.0 - 36.2
11	0.7 km NE	20.1	81.4	0.0 - 581.6
12	1.8 km ESE	12.3	49.9	0.5 - 497.8

Source: Based on draft data supplied by PEDCo (1978).

[a] Observations are for twelve 24-hr periods between September 24, 1978, and October 5, 1978.

[b] When duplicate quality control samples were taken at one site, the average of the two samples has been used.

Table V-5

ATMOSPHERIC EDC MONITORING DATA[a] FOR NEW ORLEANS, LOUISIANA

Site	Relation to		Average	Average	Range[b]
No.	Shell	Union Carbide	(ppb)	($\mu g/m^3$)	($\mu g/m^3$)
1	4.0 km NNW	6.0 km NNE	0.1	0.4	0.0- 1.2
2	4.0 km NW	4.0 km NNW	0.4	1.7	0.0- 6.2
3	3.0 km WNW	3.0 km NNW	0.4	1.7	0.0- 5.8
4	0.4 km SW	2.0 km NE	12.0	48.5	0.6-169.0
5	1.0 km NE	4.0 km NE	0.5	2.0	0.5- 9.1
6	6.0 km WSW	4.0 km NW	0.9	3.8	0.0- 20.7
7	3.0 km SW	0.8 km NNW	1.5	5.9	0.5- 24.3
8	2.0 km SW	1.5 km NE	2.3	9.4	0.5- 29.1
9	1.5 km S	2.0 km WNW	1.4	5.6	0.0- 17.6
10	2.0 km SE	3.0 km WNW	0.8	3.1	0.0- 13.1
11	3.0 km SSE	3.0 km WSW	0.5	1.9	0.0- 8.7
12	14.0 km S	12.0 km S	0.6	2.5	0.0- 6.4

Source: Based on draft data supplied by PEDCo (1978).

[a] Observations are for ten 24-hr periods between October 10, 1978, and October 17, 1978.

[b] When duplicate quality control samples were taken at one site, the average of the two samples has been used.

available are insufficient for estimating population exposure for all EDC producers. It is, therefore, necessary to use dispersion modeling to estimate neighboring population exposures. In keeping with the generalized nature of this study, approximate dispersion estimates were made using rough-cut Gaussian-plume techniques. Centerline, ground level, one-hour concentrations were calculated assuming a wind speed of 4 m/s and neutral ("D") stability. Based on engineering data characteristic of the production facilities, a typical stack height of 25 m was used to assess point source emissions (oxychlorination process vent and direct chlorination process vent). Fugitive and storage emissions were treated as area sources. The production area was assumed to be 0.01 km^2, and the area of storage tanks at production facilities were taken from the following equation supplied by Mascone (1978):

$$\text{Storage tank area } (\text{ft}^2) = \left[\left(\sqrt{\text{no. tanks}} - 1\right)60\right]^2$$

$$\text{where:} \quad \text{No. tanks} = \frac{\text{total production capacity in } 10^6 \text{ lb/yr}}{1.66 \times 3} .$$

Table V-6 lists the results of the dispersion modeling, giving the average 1-hr downwind concentrations. These 1-hr average concentrations were adjusted to annual average omnidirectional concentrations by first dividing them by 20 for conversion to maximum annual values, then further dividing them by 2.5 to smooth the maximum annual values with respect to direction. These factors were derived by Youngblood (1978) and are based on empirical data from studies of industrial sources similar to those modeled here. The atmospheric concentrations shown in Table V-6 are in $\mu g/m^3$. These concentrations can be converted to parts per billion (ppb) by multiplying by 0.244.

Exposure Estimates

We used the emission factors for the four sources of EDC emissions (fugitive, storage, direct chlorination vent, and oxychlorination vent) in Table V-2 to scale the generalized dispersion curves in Table V-6. In this way, we estimated atmospheric EDC concentrations as a function of distance from each plant. the atmospheric concentrations from the

155<

Table V-6

ESTIMATED ONE-HOUR AVERAGE DOWNWIND ATMOSPHERIC CONCENTRATIONS OF EDC[a] ($\mu g/m^3$)

Downwind Distance (km)	Point Source Emitter[b]	Emitter with 0.0625-km^2 Area[c]	Emitter with 0.01-km^2 Area[c]
0.30	3,400	4,000	10,000
0.45	4,800	3,400	7,700
0.60	4,400	2,900	5,700
0.75	3,700	2,500	4,300
1.00	2.700	2,000	2,900
1.25	2,100	1,600	2,200
1.60	1,500	1,200	1,600
2.50	800	720	810
4.00	410	380	410
6.00	230	220	220
9.00	120	120	120
14.00	66	64	66
20.00	39	39	39

---

[a] Assumes an emission rate of 100 g/s for each source, neutral ("D") stability atmospheric conditions with a wind speed of 4 m/s.

[b] Single stack 25 m high.

[c] Effective emission height of 10 m.

Source: Modeling data provided by P. Youngblood (EPA, 1978).

four emission sources were summed at each downwind distance to give total concentration. The point source emission concentrations of Table V-6 were used for oxychlorination and direct chlorination sources; the 0.01 km^2 emissions area concentrations were used for fugitive emissions; and linear interpolation between the 0.01 and 0.0625 km^2 area concentrations were used for storage emissions, depending on the computed storage area. The total annual average EDC concentration estimates as a function of distance from each plant were used to determine the radii at which the specified annual average concentrations (i.e., 0.01, 0.3, 0.6, 1.0, 3.0, 6.0, and 10.0 ppb) are attained in the vicinity of each plant.

The population residing within the radial distances to the concentrations specified above was estimated by SRI's computer system, BESTPOP (Suta, 1978). The population file consists of a grid of 1-km square sections that span the continental United States. This file was created by assigning the 1960 and 1970 populations to the grid network and by assuming uniform distribution of population within each of 256,000 enumeration districts. The computer software accesses the population file and accumulates residential population within radial rings specified about any given point. In addition, a rectangular map that is printed out for an area around each specified point shows the population by square kilometer.

We determined the latitude and longitude for each facility by contacting the company directly, from regional planning groups, or from other studies completed for EPA.

Table V-7 gives estimated population exposures to EDC from production facilities. The number of people exposed to concentrations of less than 0.1 ppb is underestimated because the dispersion modeling was not extrapolated beyond 30 km from any plant. The larger EDC producers are estimated to cause exposures of 0.01 to 0.1 ppb at distances beyond 30 km from their locations.

Table V-7

ESTIMATED HUMAN POPULATION EXPOSURES TO ATMOSPHERIC EDC EMITTED BY PRODUCERS

Annual Average Atmospheric EDC Concentration (ppb)	Number of People Exposed
10.0	1,700
6.00 -10.00	3,300
3.00 - 5.99	28,000
1.00 - 2.99	280,000
0.60 - 0.99	400,000
0.30 - 0.59	1,500,000
0.10 - 0.29	4,300,000
0.060- 0.099	1,900,000[a]
0.030- 0.059	3,500,000[a]
0.010- 0.029	550,000[a]
Total	12,500,000

---

[a] These are underestimates because the dispersion modeling results were not extrapolated beyond 30 km from each EDC production facility.

It is estimated that 12.5 million people are exposed to annual EDC concentrations greater than 0.01 ppb from EDC producers. Approximately 6.5 million of these are exposed to concentrations greater than 0.1 ppb.

Comparison of Monitoring and Modeling Concentrations

Monitoring data were available for three locations having EDC production plants (Calvert City, Lake Charles, and New Orleans). The monitoring data for each location are given in Tables V-3 through V-5. As has been previously describved, the monitoring data were recorded as 24-hr samples taken for 12-13 days at each plant in the period of August to October, 1978. Table V-8 averages these data for various distances from each plant and also presents the average concentrations over the three locations. The corresponding annual average dispersion modeling concentrations are also given in Table V-8. Therefore, when comparing the monitoring and modeling data, it is necessary to remember that the two are not expected to agree precisely since the monitoring data are site-specific and were recorded over a relatively short period of time while the modeling data are based on general assumptions and are intended to represent annual average conditions. Thus, the degree to which the annual and average monitoring concentrations are comparable depends in part on the local meteorological conditions during sampling, the placement of the monitoring stations, plant production during monitoring, averaging times, and assumed source configurations. It is believed that the monitoring data typify the year's average conditions.

Both monitoring and modeling data indicate that elevated concentrations of EDC occur at distances of at least 14 km from the plants. Comparisons of the monitoring and modeling data at various distances from the plants show that:

- The monitoring concentrations are approximately 20% higher than the modeling ones for distances of less than 1 km.
- The modeling concentrations are 30-70% higher than those monitored for distances of 1-4 km.

- For distances of 4-14 km, both monitoring and modeling results appear to be of about the same magnitude.

Thus, there is sufficient agreement between the monitoring and modeling concentrations to conclude that the generalized modeling analysis gives a reasonable first-cut estimate of ambient EDC concentrations near production facilities allowing estimates of potential population exposures.

Table V-8

COMPARISON OF EDC MONITORING AND MODELING ATMOSPHERIC CONCENTRATIONS (ppb)

	Monitoring Average Concentrations[a]				
Distance (km)	Calvert City[b]	Lake Charles[b]	New Orleans[b]	3-Location Average	3-Location Modeling Average[a]
0.7-1.0	2.0	36.7	6.3	15.0	13.5
1.1-1.5	c	6.0	1.4	3.7	9.1
1.6-2.0	1.0	7.0	1.6	3.1	6.5
2.1-3.0	2.1	1.1	0.7	1.3	4.3
3.1-4.0	0.9	c	0.3	0.6	2.1
4.1-5.0	c	c	c	c	1.6
5.1-6.0	c	c	0.9	0.9	1.2
14.0	c	c	0.6	0.6	0.4

---

[a] Data are the average 24-hr concentrations over 10 to 13 days for monitoring and estimated annual averages for modeling.

[b] The EDC emissions have been estimated in Table V-2 as 72.9 g/s for B. F. Goodrich, Calvert City, KY; 70.2 g/s for Conoco, Lake Charles, LA; and 119.5 g/s for Shell, New Orleans, LA.

[c] Indicates that no monitoring data were collected.

VI POPULATION EXPOSURES FROM PRODUCERS THAT USE EDC AS A FEEDSTOCK

General

In estimating human population exposures to atmospheric EDC from chemical production facilities that used EDC as a feedstock, products considered include VCM, 1,1,1-TCE (or methyl chloroform), TCE, PCE, EA, VDCM, and gasoline lead scavenger. Many of these chemicals are produced at the same facilities that produce the EDC feedstock. Exposure estimates are given for each product considered separately and also for all products combined.

Sources of Emissions

Table IV-2 lists producers that use EDC feedstock and their cpacities. The number of producers of each chemical that uses EDC as a feedstock is as follows:

Chemical	Producers Using EDC*
VCM	14
1,1,1-TCE	3
TCE	4
PCE	4
EA	3
VDCM	3
Lead scavenger	6

Table IV-4 indicates that, depending on the chemical, from 52 to 89% of the production capacity was used in 1977 for the preceding chemicals.

---

*See Table IV-2.

Because actual production data for each chemical at each plant are unavailable, we have assumed that each operates at the percent of capacities shown in Table IV-4.

Emissions

The VCM production process is well controlled to limit emissions. These controls also reduce emissions from the EDC used as feedstock. It is estimated that the EDC emission factor for VCM is 0.025% of EDC input. the EDC emission factor for other processes that use EDC as a feedstock is estimated as 0.2% of the EDC input (Mascone, 1978). The estimated EDC emissions are given in Table VI-1. It is assumed that these emissions are of a low level fugitive type resulting from leaks in valves and other processing equipment and from storage-tank evaporation.

Atmospheric Concentrations

Because so few atmospheric monitoring data exist for the vicinities of production plants that use EDC as a feedstock, it has been necessary to use dispersion modeling to estimate neighborhood population exposures. (Dispersion modeling is described in Section V.) The dispersion estimates for a 0.01-km^2 area source emitter (Table V-6) was used for assessing exposure.

Exposure Estimates

The EDC emissions given in Table VI-1 were used to scale the dispersion curve to estimate atmospheric EDC concentrations as a function of distance from each plant for each product. Concentrations were similarly estimated about each plant for emissions from all products. The tables showing annual average atmospheric EDC concentrations as a function of distance from each plant were used to determine the radii at which specified annual average concentrations (i.e., 1.0, 0.6, 0.3, 0.1, 0.06, 0.03, and 0.01 ppb) are attained. The population residing within the distances to the concentrations specified above was estimated by SRI's computer system, BESTPOP (Suta, 1978). We determined the latitudes and longitudes for each facility by contacting the company directly, by using information from regional planning

Table VI-1

ESTIMATED EDC ATMOSPHERIC EMISSIONS (g/s) FOR PLANTS THAT USE EDC AS A FEEDSTOCK

Plant[a]	Location	VCM	1,1,1-TCE	TCE	PCE	EA	VDCM	Lead Scavenger	Total
Borden	Geismar, LA	1.2							1.2
Conoco	Lake Charles, LA	2.9							2.9
Diamond	Deer Park, TX			0.7	1.6				2.3
Diamond	La Porte, TX	4.1							4.1
Dow	Freeport, TX	0.8	5.6	2.0		2.7	2.3		13.4
Dow	Oyster Creek, TX	2.9							2.9
Dow	Plaquemine, LA	5.1	3.7						8.8
duPont	Antioch, CA						2.3	1.1	3.4
duPont	Deepwater, NJ							1.1	1.1
Ethyl	Baton Rouge, LA	1.4		0.6	0.5			1.1	3.6
Ethyl	Houston, TX							1.1	1.1
Goodrich	Calvert City, KY	4.1							4.1
Houston	Beaumont, TX							0.9	0.9
ICI America	Baton Rouge, LA	1.2							1.2
Nalco	Freeport, TX							0.3	0.3
PPG	Lake Charles, LA	1.3	4.3	2.7	1.9		1.5		11.7
PPG	Guayanilla, PR	2.1							2.1
Shell	Deer Park, TX	3.4							3.4
Shell	Norco, LA	2.9							2.9
Stauffer	Carson, CA	0.7							0.7
Union Carbide	Taft, LA					3.2			3.2
Union Carbide	Texas City, TX					2.7			2.7
Vulcan	Geismar, LA				1.5				1.5
	Total	34.1	13.6	6.0	5.5	8.6	6.1	5.6	79.5

---

[a] Blanks indicate the chemical is not manufactured at the plant in question or that the plant has no EDC emissions.

Source: SRI estimates.

groups, or from other studies completed for EPA. The population exposures to EDC for individual products that require EDC as a feedstock are given in Table VI-2.

VCM production results in the largest number of exposures -- about 1.3 million people -- about half of all the exposures for products using EDC as a feedstock.

Table VI-3 gives the total exposures from all EDC feedstock producers for all products. As shown in Table IV-2, many facilities produce several products requiring EDC. Thus, two alternative estimates of total exposures are given in Table VI-3: Alternative A combines all the emissions reported in Table VI-1 and then uses these combined emissions to estimate total exposures about each plant. Alternative B is a summation of the individual product exposures shown in Table VI-2. Because Alternative B counts some people twice (or more times), it results in an overestimate of total exposures; however, the exposure concentrations are lower than for Alternative A.

Table VI-2

ESTIMATES OF POPULATION EXPOSURES TO ATMOSPHERIC EDC EMITTED BY PLANTS THAT USE EDC AS A FEEDSTOCK IN VARIOUS PRODUCTS

Annual Average Atmospheric EDC Concentration (ppb)	Product						
	VCM	1,1,1-TCE	TCE	PCE	EA	VDCM	Lead Scavenger
0.600-0.999	1,300						
0.300-0.599	360				70		
0.100-0.299	30,000	1,700	390	80	17,000	270	1,900
0.060-0.099	42,000	16,000	10,000	500	8,000	3,400	3,400
0.030-0.059	260,000	83,000	47,000	17,000	43,000	34,000	25,000
0.010-0.029	940,000	170,000	140,000	250,000	37,000	90,000	350,000
Total	1,300,000	260,000	200,000	270,000	110,000	130,000	380,000

Table VI-3

ESTIMATES OF TOTAL POPULATION EXPOSURES TO ATMOSPHERIC EDC EMITTED BY PLANTS THAT USE EDC AS A FEEDSTOCK

Annual Average Atmospheric EDC Concentration (ppb)	Alternative A Sum of Emissions[a]	Alternative B Sum of Exposures[b]
0.600-0.999	1,300	1,300
0.300-0.599	2,100	430
0.100-0.299	110,000	51,000
0.060-0.099	210,000	83,000
0.030-0.059	520,000	510,000
0.010-0.029	1,500,000	2,000,000
Total	2,300,000	2,600,000

---

[a] Exposures are based on the total feedstock emissions for each plant given in Table V-1.

[b] Exposures are based on the sum of the exposures for each product given in Table V-2.

VII POPULATION EXPOSURES FROM EDC IN AUTOMOBILE GASOLINE

General

Leaded gasoline contains EDC as a lead scavenger, with the amount of EDC depending on lead content. Catalytic converters were first required for the 1975 model year. In that year, 100% of Ford and GM cars and 96% of Chrysler cars required unleaded gasoline. In 1976, approximately 20% of the gasoline sold in the United Satats was unleaded (Ethyl Corporation, 1976).

The antiknock "motor mix" added to gasoline is a combination of ethylene dibromide (EDB), EDC, lead, and other alkyl groups. Quantities of EDC and EDB are used sufficient to supply two atoms of chlorine and one atom of bromine for each atom of lead. Major gasoline antiknock mixes (which are added in small quantities to leaded gasoline) typically contain 18.8% EDC by weight and 17.9% EDB by weight (SRI estimates). Whereas the current average lead content in all gasoline is 1.5 g/gal,* leaded gasoline contains approximately 2.5 g/gal. According to EPA's phase-down schedule for lead, the average lead content for all gasoline is expected to be 0.5 g/gal by 1 October 1979 (Stolpman, personal communication, 1977). Because of the low lead content in unleaded gasoline (approximately 0.01 g/gal), EDC is not required and is not added. Therefore, our analysis of population exposures related to gasoline use considers only leaded gasoline. If we assume that gasoline contains 0.425 units of EDC per unit of lead (by weight), this results in an estimated 1.1 g of EDC per gallon of leaded gasoline, or 0.02% EDC by volume.

---

*We have used gallons rather than liters to represent gasoline volume since these are the units commonly used in the United States for gasoline sales.

We evaluate nonoccupational population exposures to atmospheric emissions of EDC from leaded gasoline for three sources:

- Exposures to people who refuel their automobiles at self-service stations
- Exposures to people who reside in the vicinity of service stations
- General urban population exposures from the evaporation of EDC from automobiles.

Exposures from Self-Service Operations

Sources of Emissions

Service station types are characterized by the services they offer and their business operations; they include (1) full-service stations, (2) split-island stations, (3) self-service stations, and (4) convenience store operations. In full-service stations (1), attendants offer all services, including gasoline pumping and other mechanical check-ups. If fuel is obtained at any class of stations (2) through (4), the customers themselves may fill their tanks. In split-island stations (2), both self-service and full-service are offered. At stations (3) and (4), only self-service is available.

While pumping gasoline, an individual is exposed to EDC released as vapor from the gasoline tank.* Although occupants in the car at both self-service and full-service operations are exposed to some EDC, the highest exposures are to the person pumping the gas. Because it is difficult to estimate level and length of exposure for car occupants, only those who pump gasoline from self-service pumps are considered

---

*Vapor recovery systems affixed to the gasoline nozzle can reduce exposure levels significantly if they are working properly and are operated correctly. Such systems are required for service stations in parts of California.

here. (Note it is not within the scope of this report to evaluate occupational exposures.)

Self-service sale of gasoline is a relatively new marketing method pioneered by independent operators in the West Coast and in the southern United States. Today, it accounts for 30% of gasoline sold. The national market share of the major gasoline producers has decreased recently as independents and others specializing in high-volume, low-margin sales capture a larger percentage. Of the approximately 184,000 conventional service stations with some self-service operations account for 39% (Arthur D. Little, 1977). Table VII-1 indicates the types of service stations offering self-service gasoline.

Table VII-1

SELF-SERVICE OPERATIONS

Outlets Offering Self-Service	% of U.S. Total
Total self-service	9
Split island with self-service	26
Convenience stores	4
Total outlets with self-service	39

Source: Arthur D. Little (1977)

An Arthur D. Little report (1977) revealed that 71,300 outlets offer self-service gasoline. Gasoline sold at U.S. service stations for the year ending May 30, 1977 equalled approximately 87.4 x 10^9 gal. Of that amount, 27.0 x 10^9 gal (31%) is estimated to have been dispensed at self-service pumps. The market share of self-service stations was surveyed for four metropolitan Air Quality Control Regions (AQCR): Boston, Dallas, Denver, and Los Angeles. The market share held by self-service operations varied from 9% in Boston to 45% in Denver (see Table VII-2). Another study by Applied Urbanetics, Inc. (1976) surveyed Baltimore and Madison, Wisconsin. The results of that study

Table VII-2

GASOLINE MARKET SHARE OF SELF-SERVICE STATIONS IN FOUR AQCRs SPRING 1977

Type of Operation	Number of Outlets	Sales Volume (10^6 gal/yr)	Market Sharing Percent
Boston AQCR			
Full-service	2,253	1,045.1	91.0
Self-service (total)	100	108.6	9.0
Split island	8[a]		
Self-service	92		
Convenience stores	--		
Dallas AQCR			
Full-service	2,094	924.6	61.0
Self-service (total)	1,124	593.8	39.0
Split island	480[a]		
Self-service	444		
Convenience stores	200		
Denver AQCR			
Full-service	621[b]	292.1	55.0
Self-service (total)	656	235.7	45.0
Split island	310[a]		
Self-service	226		
Convenience stores	120		
Los Angeles AQCR			
Full-service	2,518	2,472.6	53.0
Self-service (total)	4,780	2,154.8	47.0
Split island	3,632[a]		
Self-service	1,022		
Convenience stores	126		

---

[a] Split-island operations offering full service and self-serve islands.

[b] Of these, 445 are split-island operations that offer full service and mini-serve (attnedant-operated) islands.

Source: Arthur D. Little (1977).

are shown in Table VII-3. It appears that self-service operations account for about 40% of the market in urban areas.

Emissions

To estimate the people exposed to EDC from service stations, several assumptions were necessary. The gasoline pumped through self-service outlets is estimated at 27.0×10^9 gal/yr. The annual average fuel consumption per vehicle is 736 gal (DOT, 1974a). If it is assumed that on the average, a person who primarily uses self-service gasoline makes one trip per week to the gasoline station, an average fill-up amount of 14 gal is determined by dividing 736 gal/vehicle/yr by 52 wk/yr. By dividing the average fill-up into the self-service gallons pumped, we estimate trips per year to self-service operations at 1.9×10^9. When this number is divided by 52 trips per person per year, the people exposed to pumping self-service gasoline is estimated at 37×10^6. We can further assume that only 80% of these people are pumping leaded gasoline containing EDC. Therefore, the people exposed from this source is estimated to be 30×10^6. For this estimate of the population exposed, we assume that the individuals using self-service gasoline obtain all of their gasoline at self-service stations.

Atmospheric Concentrations

A rough estimte of EDC exposures was made by extrapolating the results of the Battelle (1977) benzene monitoring. In that study, three samples of ambient air were taken in the breathing zone of persons filling their tanks at self-service gasoline stations. The results, shown in Table VII-4, indicate a wide range in the benzene concentrations of the emissions. The variations seem to be related to the subject's position in relation to the tank opening and the wind direction. Because all measurements were taken on the same day and at approximately the same time, ambient temperature did not cause the variation. Basically, if the subject was downwind of the tank opening, higher levels were recorded.

Table VII-3

GASOLINE MARKET SHARE OF SELF-SERVICE STATIONS IN TWO METROPOLITAN AREAS, 1976

Type of Operation	Sales Volume (10^6 gal/yr)	Market Sharing Percent
Baltimore SMSA		
Full-service	111.5[a]	55.0
Self-service (total)	90.5	45.0
Split island	25.5	
Self-service	65.0	
Madison SMSA		
Full-service	56.0[a]	42.0
Self-service (total)	77.0	58.0
Split island	17.0	
Self-service	60.0	

---

[a] Includes the sales from mini-serve (attendant-operated) stations and 50% of the sales from split islands.

Source: Applied Urbanetics, Inc. (1976).

Table VII-4

SAMPLING DATA FROM SELF-SERVICE GASOLINE PUMPING

Customer	Sampling Rate (mL/min)	Nozzle Time (min)	Gallons Pumped	Sample Volume (L)	Benzene Level	
					g/m^3	ppb
1	31	2.5	14	78	115	43
2	31	1.1	8	34	324	121
3	31	1.6	9	50	1,740	647

Source: Battelle (1977).

No EDC monitoring data obtained in the vicinity of gasoline stations are available. therefore, by determining the evaporation rate of EDC with respect to benzene, benzene monitoring data can be used to provide a rough estimate of EDC exposures. It is known that the evaporation rate is proportional to the vapor pressure, solubility, and the square root of the molecular weight. Thus, the following equation can be used to estimate the EDC emission factor (or emission rate) related to evaporation:

$$\frac{E_e}{E_b} \alpha \frac{P_e S_e \sqrt{m_e}}{P_b S_b \sqrt{m_b}} \qquad (7.1)$$

where the subscript e refers to EDC and the subscript b refers to benzene; E is the emission rate (or emission factor); P is the vapor pressure; S is the solubility; and m is the molecular weight.

For an estimation, (s) $(\sqrt{m})$ may be approximated by χ, the molar fraction or concentration. thus, Equation (7.1) can be written as follows:

$$\frac{E_e}{E_b} \alpha \frac{P_e \chi_e}{P_b \chi_b} \qquad (7.2)$$

The Battelle benzene monitoring data were taken when the temperatures was about 20°C. Because the vapor pressures for EDC (70 mm) and benzene (80 mm) at 20°C are known, and the volume concentrations of EDC (0.02%) and benzene (2.0%) in gasoline are also available, the emission factor (or emission rate) of EDC can be estimated by the following equations:

$$E_e = \frac{70}{80} \times \frac{0.02}{2.0} E_b \qquad (7.3)$$

$$E_e = 0.009 E_b \quad . \qquad (7.4)$$

This factor can be used to scale benzene atmospheric concentrations (g/m^3) to corresponding EDC concentrations becuse it is assumed that atmospheric concentrations are proportional. the corresponding EDC exposures were estimated, based on these data and are given in Table VII-5.

Table VII-5

ESTIMATES OF EDC EXPOSURES FROM SELF-SERVICE GASOLINE PUMPING

Customer	Nozzle Time (min)	Gallons Pumped	Estimated EDC Level g/m^3	Estimated EDC Level ppb
1	2.5	14	1.04	0.27
2	1.1	8	2.91	0.71
3	1.6	9	15.66	3.83

Average nozzle time = 1.7 min
Time weighted average exposure = 1.45 ppb

Source: SRI estimates based on Battelle monitoring data (1977). the conversion is based on Equation (7.4).

Exposure Estimates

The estimated exposure levels are based on the information contained in Table VII-5. It is recognized that these data are limited and highly variable. However, they do allow a reasonable estimate of expected exposure levels from self-service gasoline pumping. In states where vapor recovery systems are used, the estimated exposure level may be much lower. Approximately 30 x 10^6 persons use self-service stations. While filling their tanks once a week, they are exposed to an estimated EDC level of 1.5 ppb for 2.5 min (time required to pump 14 gal). Their annual exposure is estimated at 2.2 hr. This equates to an annual averge time-weighted exposure of 0.0004 ppb.

Exposures in the Vicinity of Service Stations

Sources of Emissions

People residing in the vicinity of service stations may be exposed to EDC from the evaporation of gasoline pumped by attendants and customers, and from gasoline loaded by distribution trucks. These exposures are in addition to those assessed previously for persons using self-service gasoline stations. The amount of EDC emitted depends on the ambient temperature, vapor recovery controls, the EDC content in gasoline, and the volume of leaded gasoline pumped. Approximately 80% of the gasoline currently sold is leaded. With approximately 184,000 service stations in the United States, it is expected that many people are exposed to EDC from those sources. Because most service stations are located in urban areas and because their location is expected to be highly correlated with urban population density, only urban areas are considered in this analysis.

Emissions

An EDB emission factor of 0.00157 g of EDB per gram of lead per gallon from refueling losses has been estimated, based on testing at EPA's Mobile Source Air Pollution Control Laboratory in Ann Arbor, Michigan (Kittredge, 1977). The factor considers spilling, vapor displacement, entrained liquid gasoline losses, and volume of gasoline pumped. Assuming an average lead content in gasoline of 2.5 g/gal, the estimated emission factor for EDB is 0.00039 g/gal. The EDB emission factor can be used to estimate the EDC emission factor through the use of Equation (7.2) (and by substitution of EDB factors for benzene factors in the equation). We have assumed that the EDB vapor pressure is 12 mm at 25°C and that it constitutes 0.05% of the gasoline (by volume). Hence, we estimte that the EDC emission factor for automotive refueling losses (E_e) is:

$$E_e = \frac{80}{12} \times \frac{0.02}{0.05} \times 0.00039 = 0.001 \text{ g/gal.} \tag{7.5}$$

The number of service stations in urban areas can be estimated, based on urban service station density and total U.S. urban population. Service station density in urban areas can be extrapolated from the data presented in Table VII-6. The service station density shown for four metropolitan AQCRs varies, with no regional pattern evident. Based on these data, we estimate an average of 0.7 service stations per 1,000 population. This number can be applied generally to urban areas throughout the United States. Urbanized areas[*] provide the best population base. The 1970 population residing in urbanized areas was 118,447,000 (Bureau of the Census, 1975). Thus, service stations in urbanized areas are estimated at 83,000, or 45% of all stations.

An emission rate can be estimated by employing the following assumptions:

(1) 70.0×10^9 gal of leaded gasoline are sold annually by service stations.

(2) The average number of gallons pumped per service station is 3.8×10^5 gal. (The United States has approximately 184,000 service stations.)

---

[*] Defined by the Bureau of Census as the central city or cities and surrounding closely settled territories. All sparsely settled areas in large incorporated cities are excluded by this definition. Densely populated suburban areas, however, are included (U.S. Department of Commerce, Bureau of the Census, 1972 County and City Data Book).

Table VII-6

SERVICE STATION DENSITY IN FOUR METROPOLITAN AQCRs

AQCR	Number of[a] Service Stations (1977)	AQCR[b] Population (1975)	Service Stations[c] per 1,000 Population
Boston	2,353	4,039,800	0.6
Dallas	3,218	2,970,900	1.1
Denver	1,277	1,389,000	0.9
Los Angeles	7,298	14,072,400	0.5

Sources:

[a] A. D. Little (1977).
[b] Bureau of Economic Analysis (1973)
[c] SRI estimates.

(3) All service stations have uniform pumping volumes.

(4) The EDC emission rate for a service station is:

(Vol. of gasoline pumped)(emission factor) = emission rate; that is, (3.80×10^5 gal/yr)(0.001 g/gal) = 380 g/yr = 1.2×10^{-5} g/s.

Atmospheric Concentrations

Dispersion modeling of benzene emissions from gasoline service stations (Youngblood, 1977) employed the Single Source (CRSTER) Model (USEPA, 1977). Meteorological data for Denver, Colorado were used to represent a reasonable worst-case location. EDC emissions from gasoline service stations are thought to be from sources similar to those for benzene. The dispersion modeling assumed that the sources of emissions are dispersed over a 50 sq ft area. The benzene concentrations of the previous study were modified to reflect EDC emissions by first multiplying the benzene concentrations (ppb) by 3.2 to convert them to $\mu g/m^3$ and then by multiplying the $\mu g/m^3$ by 0.244 to convert to ppb of EDC.

Table VII-7 presents the results of the benzene modeling modified for EDC; an EDC emission of 0.01 g/s is assumed. Two conditions are given: (1) the 8-hr worst-case concentrations for a service station that operates only during daytime, and (2) the annual average concentrations for a service station that operates 24 hr/day.

Exposure Estimates

Population exposures to EDC emissions from gasoline service stations have been estimated by assuming that the population in urbanized areas is uniformly distributed with a density of $1,318/km^2$ (based on the 1970 census). We have also assumed that no one resides within 50 m of a gasoline service station. To calculate atmospheric concentrations as a function of distance, the annual average dispersion modeling data in Table VII-7 were scaled by the estimated EDC emissions

Table VII-7

ROUGH DISPERSION MODELING RESULTS FOR EDC EMISSIONS
FOR GASOLINE SERVICE STATIONS[a]

Distance (m)	8-hr Worst Case (ppb)[b]	Annual Average (ppb)[c]
50	12	1.0
100	6	0.5
150	3	0.3
200	2	0.2
300	1	0.1

---

[a] Assumes an EDC emission of 0.01 g/s during operation.

[b] Assumes continuous operation from 8 a.m. to 4 p.m., 6 days per week.

[c] Assumes continuous operation 24 hr per day, 7 days per week.

Source: Modified from Youngblood (1977) by adjusting ppb of benzene to ppb of EDC.

of these sources have been treated as point sources and their emissions are evaluated elsewhere in this report. This section presents analysis of exposures due to emissions of EDC from automobiles.

Emissions

As previously discussed, the EDC content in leaded gasoline averages 0.02% by volume, and leaded gasoline accounts for 80% of all gasoline sold. Tests by EPA's Mobile Source Air Pollution Control Laboratory in Ann Arbor, Michigan, have indicated that EDB is destroyed in the combustion process (Kittredge, personal communications, 1977), and it has been calculated that EDC is similarly destroyed (Mabey, 1978). However, evaporation from the carbureator and from the fuel tank does occur. We have been unable to locate data on EDC emissions from this type of evaporation; however, data are available for tests measuring EDB (Table VII-8).

Table VII-8

AUTOMOTIVE EDB EMISSION FACTORS
(G/G OF LEAD PER GALLON OF GASOLINE)

Vehicle Type	Low	High
Uncontrolled vehicle (pre-1972)	0.00144	0.00362
Pre-1978 controlled vehicle	0.00098	0.00250
Post-1978 controlled vehicle	0.00033	0.00085

Source: Kittredge, 1977

The average EDB emission factor for uncontrolled vehicles, based on Table VII-8, is 0.00253 g of EDB per gram of lead per gallon. Assuming 2.5 g of lead per gallon of leaded gasoline, the estimated EDB emission factor is 0.0063 g of EDB per gallon. The EDB emission factor can be used to estimate the EDC emission factor through the use of Equation (7.2). By substitution in this equation, the EDC emission factor (E_e) for uncontrolled automobile evaporation becomes:

182<

$$E_e = \frac{80}{12} \times \frac{0.02}{0.05} \times 0.0063 = 0.017 \text{ g of EDC/gal} \qquad (7.6)$$

This factor will provide a slightly high estimate of ambient EDC levels because it assumes all automobiles using leaded gasoline have emissions comparable to pre-1972 models. In fact, the 1975 model year was the first in which automobiles were required to run on unleaded gasoline, but controls to reduce carbureator evaporation were introduced in the 1972 model year.

Dispersion Modeling

The Hanna-Gifford area-wide dispersion model (Gifford and Hanna, 1973) as applied by Schewe (1977) for benzene is used for this analysis and modified for EDC. Mara and Lee (1978) contains a discussion of this model and its application to benzene. Because EDC is destroyed during combustion (Mabey, 1978), only evaporation is considered. The modified equation to estimate the emission rate for EDC is as follows:

$$Q_{evap} = (0.017 \text{ g/gal}) \left(\frac{\text{annual travel miles/vehicle}}{\text{average miles/gal}} \right) (\text{vehicles registered}) \frac{1}{\text{area}} \qquad (7.7)$$

If 12,000 mi/yr for each vehicle and 12 mi/gal are assumed (DOT, 1974b), the above equation becomes

$$Q_{evap} = (5.4 \times 10^{-7} \text{ g/s}) \times \left(\frac{\text{vehicles registered}}{\text{area}} \right) \qquad (7.8)$$

To calculate the annual average areawide EDC concentration, the following equation is used:

$$\chi_A = \frac{225\, Q_{evap}}{u} \qquad (7.9)$$

where u is wind speed (m/s) and χ_A is the atmospheric concentration in g/m^3. The average annual wind speed, u, in the area of study was obtained from AP101 (EPA, 1972). Because wind speed (and thus dispersion) increases in the afternoon, the morning values were used to estimate higher concentrations. the number 225 is an empirical factor derived from several studies that give very good results for long-term averages for low-level emission sources (Gifford and Hanna, 1973).

Estimates of Exposures

Cities whose vehicular densities are higher should have the higher EDC concentration from automobile evaporation. Because 916 cities in the United States have populations greater than 25,000, we used a statistical sampling approach to evaluate EDC exposures. Table VII-9 shows the distribution of cities by size. Because of the expected higher EDC concentratons in the larger cities, it was decided to evaluate the exposures for the 26 cities with populations greater than 500,000 and to do a fractional sample of the cities in the smaller groups. However, because vehicle registration data were unavailable for Boston and New Orleans, only 24 of the largest 26 cities were evaluated. Of the cities in the 250,000-500,000 size range, 25% were

Table VII-9

DISTRIBUTION OF CITIES BY 1970 POPULATION

Population Size	Number of Cities	Combined Population
1,000,000	6	18,769,000
500,000-1,000,000	20	12,967,000
250,000- 500,000	30	10,442,000
100,000- 250,000	100	14,286,000
50,000- 100,000	240	16,724,000
25,000- 50,000	520	17,848,000

Source: U.S. Bureau of the Census, Statistical Abstracts of the United States-1974.

sampled, as were 15% of the cities in the 100,000 to 250,000 size range. No EDC exposures greater than 0.01 ppb were estimated for cities with population less than 100,000. Exposures were estimated for people within the sample, and these sampling results were then projected to all cities, based on the ratio of total population to sample population.

Table VII-10 sets forth the exposure estimates for the cities sampled. No exposures were found to exceed 0.03 ppb. Table VII-11 gives the calculations used to project the sampling data to the total population. Based on this projection we estimate that approximately 13 million people are exposed to annual average EDC concentrations of 0.01 to 0.03 ppb from the evaporation of gasoline from automobiles.

Summary of Urban Exposures from Automobile Gasoline

Exposures to EDC from leaded gasoline have been estimated for people refueling their automobiles at self-service stations, for those residing near service stations, and for those exposed to EDC evaporation from automobiles. We estimate that approximately 30 million people are exposed to an EDC concentraton of 1.5 ppb for 2.2 hr/yr while refueling their automobiles. Approximately 600,000 to 1,400,000 (average of 1 million) people residing near gasoline service stations are exposed to annual average EDC concentraions of 0.01 to 0.03 ppb from refueling losses. Another 13 million people are exposed to annual average EDC concentrations of 0.01 to 0.03 ppb from automobile evaporation.

Table VII-10

ESTIMATED U.S. CITY EXPOSURES TO EDC FROM THE EVAPORATION OF AUTOMOBILE GASOLINE

Rank	Name	Population[a] (1,000)	Automobiles[b] (1,000)	Q_{evap}[c] (10^{-10} g/s-m^2)	Wind Speed (m/s)	Concentration (ppb)
1	New York, NY	7,895	1,707	11.9	7	0.01
2	Chicago, IL	3,363	1,476	13.8	5	0.01
3	Los Angeles, CA	2,816	1,515	6.8	3	0.01
4	Philadelphia, PA	1,949	954	15.5	6	0.01
5	Detroit, MI	1,511	796	12.0	6	0.01
6	Houston, TX	1,232	692	3.3	6	0.01
7	Baltimore, MD	906	412	11.0	6	0.01
8	Dallas, TX	844	741	5.8	6	0.01
9	Washington, DC	757	391	13.3	5	0.01
10	Cleveland, OH	751	392	10.8	5	0.01
11	Indianapolis, IN	746	237	1.9	5	0.01
12	Milwaukee, WI	717	328	7.2	5	0.01
13	San Francisco, CA	716	367	16.9	3	0.02
14	San Diego, CA	697	388	2.6	3	0.01
15	San Antonio, TX	654	333	3.8	6	0.01
17	Memphis, TN	624	306	2.9	5	0.01
18	St. Louis, MO	622	295	10.1	6	0.01
20	Phoenix, AZ	582	357	3.0	4	0.01
21	Columbus, OH	539	334	5.2	5	0.01
22	Seattle, WA	531	273	6.8	5	0.01
23	Jacksonville, FL	529	355	1.0	6	0.01
24	Pittsburgh, PA	520	252	9.5	5	0.01
25	Denver, CO	515	331	7.3	4	0.01
26	Kansas City, KA	507	264	1.7	6	0.01
27	Atlanta, GA	497	354	5.6	5	0.01
32	Minneapolis, MN	434	237	9.0	6	0.01
37	Oklahoma City, OK	367	238	0.8	6	0.01
42	Miami, FL	335	221	13.4	6	0.01
47	Norfolk, VA	308	144	5.7	7	0.01
52	Akron, OH	275	153	5.9	6	0.01
57	Richmond, VA	250	132	4.6	5	0.01
62	Corpus Christi, TX	204	102	2.1	6	0.01
72	Ft. Wayne, IN	178	112	4.5	5	0.01
82	Fresno, CA	166	86	4.3	3	0.01
87	Santa Ana, CA	157	98	7.6	3	0.01
92	Lubbock, TX	149	80	2.2	6	0.01
97	Riverside, CA	140	73	2.1	3	0.01
112	Peoria, IL	127	66	3.7	5	0.01
117	Macon, GA	122	72	3.1	5	0.01
122	Savannah, GA	118	63	4.9	5	0.01
127	Columbia, SC	114	63	1.2	5	0.01
132	Alexandria, VA	111	57	8.1	5	0.01
137	Allentown, PA	110	58	6.8	3	0.01
142	Hollywood, FL	107	82	6.8	5	0.01
151	Duluth, MN	101	45	1.4	6	0.01
157	Pueblo, CO	97	50	4.6	4	0.01
162	Sunnyvale, CA	95	55	5.4	3	0.01

---

[a] 1970 census city population.

[b] Registered automobiles by SMSA as given in DOT (1974b) have been assigned to cities, based on the ratio of city population to SMSA population.

[c] See Equation (7.8).

Table VII-11

CALCULATIONS OF NATIONAL EXPOSURES[*] TO EDC FROM AUTOMOBILE EVAPORATION

City Population	Total U.S. Population	Population Sampled	Fraction Sampled Exposed to 0.01 ppb	Projected Population Exposures 0.01 ppb
1,000,000	18,769,000	18,769,000	0.43	8,130,000
500,000-1,000,000	12,967,000	11,733,000	0.19	2,460,000
250,000- 500,000	10,442,000	2,670,000	0.13	1,310,000
100,000- 250,000	14,286,000	1,892,000	0.08	1,140,000
	Total			13,040,000

---

[*] All exposures are in the 0.01 to 0.03 ppb range.

VIII OTHER ATMOSPHERIC EXPOSURE ROUTES

General

Environmental exposures to EDC may occur through any of its dispersive uses, including grain fumigants, paints, coating, adhesives, cleaning, and the prepartion of polysulfide compounds. Additional environmental exposures may occur from spills and venting during transportation and from evaporation at waste disposal operations. Few data are available on the amount of EDC used or lost to the environment from these potential exposure routes; consequently, only qualitative descriptions of exposures can be given.

Dispersive Uses

Auerback Associates, Incorporated (1978) estimated consumption of EDC for minor uses in 1977 at about 5,000 mt. Of this total, about 28% (1,400 mt) was used in the manufacture of paints, coatings, and adhesives. Extracting oil from seeds, treating animal fats, and processing pharmaceutical products required 23% of the total (1,150 mt). An additional 19% (950 mt) was consumed cleaning textile products and PVC manufacturing equipment. Nearly 11% (550 mt) was used in the preparation of polysulfide compounds. Grain fumigation required about 10% (500 mt). The remaining 9% (450 mt) was used as a carrier for amines in leaching copper ores, in the manufacture of color film, as a diluent for pesticides and herbicides, and for other miscellaneous purposes. It is generally assumed that all of this material is eventually released to the atmosphere (Drury and Hammons, 1978).

Atmospheric exposures to EDC from these dispersive uses occur as point source losses from the industrial sites where these products are manufactured and from the use of end products.

Atmospheric dispersion modeling* was used to provide crude estimates of magnitude of exposures that might be attained from the manufacture of these other products. Use of the dispersion modeling has shown that a plant would have to use more than 90 mt/yr of EDC to have concentrations in excess of 0.01 ppb at the assumed plant boundary 0.5 km from the plant center. A plant that uses 1,000 mt/yr of EDC would have concentrations of 0.1 ppb at the plant boundary (0.5 km) and 0.01 ppb at 2.5 km from the emissions. Production data are not available for these dispersive uses. Since a total of 5,000 mt/yr are involved in all dispersive uses, it is highly unlikely that any one production plant would use as much as 1,000 mt/yr of EDC. Based on these preliminary calculations, it appears that the EDC exposures to people residing near these other manufacturing plants are minimal.

Nonoccupational exposures from end product use would occur primarily from the use of paints, coatings, adhesives, and solvents, and to people who inadvertently enter fumigated areas. All of these exposures would be intermittent and are extremely difficult to estimate.

Transportation

EDC may be emitted to the atmosphere during transportation from inadvertent spills and from venting. The amount of EDC transported each year is not well known because companies transport the chemical between their plants as well as to other companies or to places for export to other countries. We estimate that at least 672,000 mt of EDC were transported during 1977 (approximately 13% of production). This includes 5,000 mt required for minor dispersive uses, 177,000 mt for exportation, and an estimated 490,000 mt transported within the United States for use in the major products shown in Table IV-2. The estimated

---

*For the modeling, it has been assumed that EDC emissions are 1% of input and that the emissions occur over a 0.01 km^2 area (see Table V-6).

490,000 mt transported for major product use was obtained as the sum of shortages between EDC production and EDC required at individual plants. We assumed that each plants' production, for each product, was at the total capacities given in Table IV-2 times the percent capacities used during 1977 (Table IV-4). However, a chemical plant is flexible in regard to the products it actually makes, and this factor could result in considerably more EDC actually being transported than estimated.

The major transportation emissions would probably result from venting and spillage during loading and unloading transportation containers. Thus, these emissions would occur at the processing plants and would add to the EDC emissions from other plant activities. Other emissions could result from venting while in transport and from accidental rupture of a container.

No data are available on EDC emissions during loading and unloading; however, Mara and Lee (1978) give uncontrolled emission factors for the transfer of benzene (Table VIII-1) by inland barge, tank truck, and rail car. The benzene emission factors can be adjusted to rough order EDC emission factors by adjusting for the differences in vapor pressure through the use of Equation (7.2). This adjustment gives an uncontrolled EDC emission factor of approximately 10 g/gal or 0.18% by weight. This must be regarded as an upper limit because some of the

Table VIII-1

SUMMARY OF UNCONTROLLED EMISSION FACTORS FOR THE TRANSFER OF BENZENE

Operation	Benzene Emission Factor (g/gal)
Inland barge	0.76
Tank truck	1.8
Rail car	1.8
Average	1.45

Source: Compiled by Mara and Lee (1978)

transfer areas have controls. If we assume that 672,000 mt of EDC are transported each year, that emissions might occur during loading and unloading, and that the emission factor is less than 0.18%, an extreme upper emission estimate of 2,400 mt/yr results.

Waste Disposal

EDC wastes may be generated in any process in which the chemical is involved. The largest quantities of EDC wastes occur during the synthesis of the compound and in the production of VCM, processes that involve all of the EDC production and most of its consumption. The treatment of wastes is of concern in estimating atmospheric emissions because of EDC's moderately high volatility (see Section III).

Liquid wastes result from scrubbing vented gases or crude EDC with water or caustic solutions. The treatment of these wastes varies from plant to plant, but usually this wastewater is used for pH control in other processing areas or is sent off site for final processing (EPA, 1974).

Solid wastes are usually disposed of by burial in a landfill or by incineration (Patterson, 1975). Solid wastes also occur in EDC manufacturing plants that use fluidized bed, rather than fixed bed, reactors (EPA, 1974). These solid wastes are periodically removed from the rejected water settling ponds and transported to landfills.

Monsanto Research Corporation (1975) has estimated EDC emission factors emitted to solid waste and water for EDC formulation. We have used Monsanto's conclusions, shown in Table VIII-2, to estimate that during 1977, 10,600 mt were discharged to solid wastes and that 18,500 mt were discharged to water. Additional solid waste and water discharges occur as a result of production of chemicals that used EDC as a feedstock.

Table VIII-2

ESTIMATED 1977 EDC EMISSIONS AS SOLID WASTE AND TO WATER FROM EDC PRODUCTION

	Solid Waste	Water
Emission Factor[a] (kg/mt)		
Direct chlorination	1.5	2.9
Oxychlorination	2.8	4.6
Emissions[b] (1,000 mt/yr)		
Direct chlorination	4.5	8.5
Oxychlorination	6.1	10.0
Total Emissions	10.6	18.5

---

[a] Based on Monsanto (1975).

[b] Assumes 58% direct chlorination and 42% oxychlorination (Patterson, 1976) and an EDC production of 5,194,000 mt/yr.

Estimating atmospheric exposures from the solid waste and water EDC emissions would require:

(1) An estimate of the rate of return to the atmosphere

(2) Identification of the contaminated sites, the amount deposited at each site, and the site's location in respect to population

(3) A method for transforming emission estimates to estimates of atmospheric exposure.

Currently, the data available on items (1) and (2) are insufficient for estimating exposures. Table II-2 indicates that an estimated 52,000 mt of EDC is emitted directly to the atmosphere annually from sources other than transportation and waste disposal. If all the EDC solid waste and water emissons evaporate to the atmosphere, an additional 29,100 mt/yr of atmospheric emissions would result. This estimate, however, is uncertain since the rate of evaporation from landfills and water emissions cannot be adequately assessed.

BIBLIOGRAPHY

Altshuller, A. P., "Lifetime of Organic Molecules in the Troposphere and Lower Stratosphere," Environ. Sci. Tech. (to be published).

Applied Urbanetics, Inc., "Market Share Study," FEA Contract No. CO-06-60435 (1976).

Arthur D. Little, Inc., "Self-Serve Market Shares in Four Metropolitan Areas," memo to Richard J. Johnson, EPA, from E. Quakenbush and P. E. Mawn (June 1977).

Auerbach Associates, "Miscellaneous and Small-Volume Consumption of Ethylene Dichloride," unpublished report prepared for EPA under Contract EPA-68-01-3899 and Auerbach Associates, Inc., AA1-2431-104-TN-1 (1978).

Battelle-Columbus Laboratories, letter to Richard J. Johnson, EPA, from C. W. Townley concerning "Results of Self-Service Exposure Samples" (May 1977).

Bureau of the Census, Statistical Abstract of the United States (1975).

Bureau of Economic Analysis, "Projections of Economic Activity for Air Quality Control Regulations," NTIS PB-259-870 (1973).

Chemical Marketing Reporter, "Profile: Ethylene Dichloride," 212(3):9 (1977).

Dilling, W., N. Tefertiller, and G. Kallos, "Evaporaton Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Chlorinated Compounds in Dilute Aqueous Solutions," *Environ. Sci. Technol. 9*:833-837 (1975).

Drury, J. S., and A. S. Hammons, "Investigations of Selected Environmental Pollutants: 1,2-Dichloroethane," Oak Ridge National Laboratory, Draft Report prepared for the Office of Toxic Substances, EPA (1978).

Ethyl Corporation, "Yearly Report of Gasoline Sales by States" (1976).

Federal Register, "Consolidation of Hazardous Material Regulations," 41(74):15972-15990 (1976).

Gifford, F. A., and S. R. Hanna, "Technical Note: Monitoring Urban Air Pollution," in *Atmospheric Environment*, Vol. 7, Pergamon Press (1973).

Grimsrud, E., and R. Rasmussen, "Survey and Analysis of Halocarbons in the Atmosphere by Gas Chromatography - Mass Spectrometry," *Atmos. Environ.* (England), *9*:1014-1017 (1975).

Hanst, P., "Noxious Trace Gases in the Air," *Chemistry 51(2)*:6-12 (1978).

Hardie, D., "Chlorocarbons and Chlorohydrocarbons," in Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Vol. 5, pp. 171-178, Interscience, New York (1964).

Hawley, G.G. (ed.), *The Condensed Chemical Dictionary*, 9th ed., Van Nostrand Reinhold Company, New York (1977).

Horvath, R., "Microbial Co-metabolism and the Degradation of Organic Compounds in Nature," *Bacteriol. Rev. 36(2)*:146-155 (1972).

Johns, R., "Air Pollution Assessment of Ethylene Dichloride," MTR-7164, The Mitre Corporation (1976).

Kittredge, G. D., memo to files concerning "Up-to-date Estimate of Automotive Emission Factors," (26 September 1977).

Mabey, W. R., Physical Organic Chemistry Laboratory, SRI International, personal communications (December 1978).

Mara, S. J., and S. S. Lee, "Assessment of Human Exposures to Atmospheric Benzene," SRI International (1978).

Mascone, D., EPA, personnel communications (16 November 1978).

McConnell, G., D. Ferguson, and C. Pearson, "Chlorinated Hyrdocarbons and the Environment," Endeavor 34:13-18 (1975).

Mitten, M., K. Dress, W. Krochta, F. Ewald, and D. DeWitt, "Chlorocarbons," in Encyclopedia of Industrial Chemical Analysis, Vol. 9, F. D. Snell and L. S. Ettre, eds., pp. 437-510, Interscience, New York (1970).

Monsanto Research Corporaton, "Potential Pollutants from Petrochemical Processes," as cited in Drury and Hammons (q.v.).

National Institute for Occupational Safety and Health, "Criteria for a Recommended Standard Occupational Exposure to Ethylene Dichloride," NIOSH-76-139 (1976).

__________, Registry of Toxic Effects of Chemical Substances, Vol. II, p.388 (1977).

__________, "Current Intelligence Bulletin #25: Ethylene Dichloride (1,2-dichloroethane)" (19 April 1978).

Patterson, R. M., M. I. Bornstein, and E. Garshick, "Assessment of Ethylene Dichloride as a Potential Air Pollution Problem," GCA Corporation (1976).

Pearson, C., and G. McConnell, "Chlorinated C_1 and C_2 Hydrocarbons in the Marine Environment," Proc. R. Soc., London, Ser. B, 189:305-332 (1975).

PEDCo, "Draft of Preliminary Monitoring Data," collected for EPA (1978).

Pellizzari, E. D., "Electron Capture Detection in Gas Chromatography," J. Chromat. 99:3-12 (1974).

Radding, S., D. Liu, H. Johnson, and T. Mill, "Review of the Environmental Fate of Selected Chemicals, SRI International, EPA-560/5-77-003, Office of Toxic Substances, EPA (1977).

Rothon, R. N., "Petroleum and Organic Chemicals," in Chemical Technology: An Encyclopedic Treatment, Vol. 4, Barnes and Noble, New York (1972).

Schewe, G. J., EPA, memos concerning "Estimates of the Impact of Benzene from Automotive Sources" to R. J. Johnson (20 June, 9 August, 12 August 1977).

Singh, H., L. Salas, and L. Cavanagh, "Distribution, Sources, and Sinks of Atmospheric Halogenated Compounds," J. Air Pollut. Control Assoc. 27(4):332-336 (1977).

Snelson, A., R. Butler, and F. Jarke, "Study of Removal Processes for Halogenated Air Pollutants," U.S. Environmental Protection Agency, EPA-600/3-78-058 (1978).

Spense, J., and P. Hanst, "Oxidation of Chlorinated Ethanes," J. Air Pollut. Control Assoc. 28(3):250-253 (1978).

196<

Stolpman, P., EPA, personal communication (October 1977).

Storck, W., "Big Chemical Producers Post Moderate Growth," _Chem Eng. News 56(18)_:31-37 (1978).

Suta, B. E., "BESTPOP: A Fine-Grained Computer System for the Assessment of Residential Population," SRI International (1978).

Toxic Materials News, "NCI Finds Ethylene Dichloride to be Carcinogenic" (27 September 1978).

U.S. Environmental Protection Agency, "Mixing Heights, Wind Speeds, and Potential for Urban Air Pollution Throughout the Contiguous United States," in Publication No. AP-101 (1972).

__________, "Engineering and Cost Study of Air Polluton Control for the Petrochemical Industry," Vol. 3, "Ethylene Dichloride Manufactured by Oxychlorination," EPA-450/3-73-006-C (1974).

__________, "Report on the Problem of Halogenated Air Pollutants and Stratospheric Ozone," EPA-600/9-75-008 (1975).

__________, "Users' Manual for Single-Source (CRSTER) Model," EPA-450/2-77-013 (1977).

__________, draft material relating to human exposure to atmospheric ethylene dichloride near production facilities (1978).

U.S. Department of Transportation, Federal Highway Administration, "Highway Statistics" (1974a).

__________, "Motor Vehicle Registrations by Standard Metropolitan Statistical Areas," Table MV-21 (1974b).

U.S. International Trade Commission, "Synthetic Organic Chemicals, U.S. Production and Sales" (1973-1977).

Whitney, W., "Fumigation Hazards as Related to the Physical, Chemical, and Biological Properties of Fumigants," Pest Control 29(7):16-21 (1961).

Windholtz, M., The Merck Index, 9th ed., Merck and Company, Rahway, New Jersey (1976).

Youngblood, P. L., EPA, memo concerning "Use of Dispersion Calculations in Determining Population Exposures to Benzene from Chemical Plants" to R. Johnson (20 September 1977).

Youngblood, P. L., "Dispersion Modeling for Determining Population Exposure to Benzene," EPA memo to R. Johnson (4 January 1978).

ASSESSMENT OF HUMAN EXPOSURES TO ATMOSPHERIC PERCHLOROETHYLENE

Final Report

January 1979

By:

Susan J. Mara
Benjamin E. Suta
Shonn S. Lee

Prepared for:

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

Task Officer: Jack K. Greer, Jr.
Project Officer: Joseph D. Cirvello

Contract No. 68-02-2835
SRI Project CRU-6780

Center for Resource and Environmental Systems Studies
Report No. 73

199<

NOTICE

This report has been provided to the U.S. Environmental Protection Agency (EPA) by SRI International, Menlo Park, California, in fulfillment of Contract 68-02-2835. The opinions, findings, and conclusions expressed herein are those of the authors and are not necessarily those of EPA. Mention of company or product names is not to be considered an endorsement by EPA.

200<

CONTENTS

LIST OF ILLUSTRATIONS iv
LIST OF TABLES v
ACKNOWLEDGEMENTS 1

I SUMMARY 2

II PERCHLOROETHYLENE IN THE ENVIRONMENT 5
  A. Introduction 5
  B. Chemical and Physical Properties of Perchloroethylene . . . 6
  C. Sources of Perchloroethylene 8

III PRODUCTION FACILITIES 15
  A. Source 15
  B. Methodology 19
  C. Exposures 25

IV DRY CLEANING OPERATIONS 28
  A. Sources 28
    1. Perc Consumption 28
    2. Process Description 30
    3. Emission Controls 31
    4. Monitoring Data 33
  B. Methodology 35
  C. Exposures 41

V METAL CLEANING OPERATIONS 46
  A. Sources 46
    1. General 46
    2. Service/Maintenance Industry Degreasing 50
    3. Manufacturing Industry Degreasing 51
  B. Methodology 53
    1. Emissions - Cold Cleaners 53
    2. Emissions - Open-Top Vapor Degreasers 53
    3. Emissions - Conveyorized Degreasing 53
    4. Perchloroethylene Emissions 55
    5. Exposure Estimates 55
  C. Exposures 58

BIBLIOGRAPHY 64
APPENDIX A Number of Dry Cleaners in Urban Areas and Exposed Population from Dry Cleaners, by State A-1

LIST OF ILLUSTRATIONS

1. Market Distribution of Perc, 1978 11

2. General Dispersion Curve for Perc Based on an Emission Rate of 1.0 Gram per Second 23

LIST OF TABLES

1. Summary of Estimated Population Exposures to Atmospheric Perc 4

2. Physical Properties of Perchloroethylene. 7

3. Estimated Consumption of Perc by Type of Use, 1978. 9

4. Summary of Ambient Monitoring Data for Perc in Various Locations 13

5. Ambient Concentrations of Perc Measured by Rutgers University, 1973-74 14

6. Locations of and Production Figures for Perc Facilities . . . 16

7. Summary of Waste Disposal Practices at Perc Production Facilities. 18

8. Results of Monitoring for Perc at Facilities Producing Trichloroethylene and Methyl Chloroform 20

9. Estimated Emissions From Perc Facilities. 21

10. Locations of Each Perc Production Facility by Latitude and Longitude 26

11. Population Exposed to Perc From Production Facilities 27

12. Perc Consumption by Type of Dry Cleaning Operation, 1978. . . 29

13. Perc Losses From Dry Cleaning Processes and Equipment 32

14. Perc Losses From Dry Cleaning Plants With Vapor Adsorbers . . 34

15. Variation in Perc Emissions Based on Type of Load for Dry Cleaning. 36

16. Perc Exposure Data for Employees in Commercial Dry Cleaning Plants 37

17. Density of Dry Cleaners in Selected Cities. 39

18. Estimated Number of Urban Dry Cleaners Using Perc by Size of Operation. 42

19. Estimated Emission Rates for Each Type of Dry Cleaning Operation 43

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the cooperation and guidance given by several individuals of the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Ken Greer, Strategies and Air Standards Division, and Dr. George H. Wahl, EPA Consultant, provided direction throughout the study. Valuable assistance concerning control technology and emission factors related to sources of perchloroethylene was provided by Charles Kleeberg, David Mascone, and Jeff Shumaker of the Emission Standards and Engineering Division. Joseph D. Cirvello was the Project Officer.

Mr. Casey Cogswell, SRI International, Chemical Industries Center, generously provided information and guidance concerning manufacuring and distribution of perchloroethylene. Ms. Lynn Manfield edited the report.

I SUMMARY

This report is one in a series that SRI International is providing for the U.S. Environmental Protection Agency (EPA) to estimate populations-at-risk to selected pollutants. The primary objective of this study was to estimate the environmental exposure of the U.S. population to atmospheric perchloroethylene (perc) emissions. The three principal sources of atmospheric perc considered in this report are facilities in which perc is produced or used as a chemical intermediate, dry cleaning operations, and metal cleaning operations.

The method of approach for estimating population exposures varied with the type of data available. Production facilities were located by latitude-longitude, and the perc emission rates for these facilities were calculated. Average annual concentrations of perc in the vicinity of these facilities were then estimated by applying approximate dispersion modeling results. The population exposed at average annual concentrations greater than 0.01 ppb was estimated.

The number of urban dry cleaning and metal cleaning operations that use perc, and the emission rates associated with them, were estimated on a state-by-state basis. Average annual concentrations were calculated through dispersion modeling based on the assumption that plants are uniformly distributed throughout urban areas and that each one will act as a point source. The number of people in each area exposed at concentrations greater than 0.05 ppb* was estimated.

The resulting estimates are subject to considerable uncertainty in regard to: (1) perc emissions from various facilities; (2) locations of sources; (3) control technologies employed; (4) deterioration of control

---

*The dispersion modeling technique was not considered valid below 0.05 ppb, because the closeness of the sources resulted in double counting of the exposed population.

technologies over time; (5) physical characteristics of perc sources;(6) the number of metal cleaning and dry cleaning operations that use perc; (7)
population density in the vicinity of sources in urban areas; and (8) living patterns of the urban population. Given these complex and variable factors, the accuracy of the estimates could not be assessed quantitatively. Despite the uncertainties, however, the estimates approximate expected conditions.

Table 1 summarizes the results of the assessment. The two largest sources of exposures are commercial dry cleaners and metal cleaning operations, each of which affect 30 million people. Metal cleaning operations are also the source of the largest number of exposures at concentrations greater than 1.0 ppb.

To facilitate approximate comparisons of different emission sources, weighted exposures have been calculated in similar units by multiplying the number of people exposed by the annual average perc concentration in each range. These values were then summed for each emission source to produce estimates expressed in ppb-person-years (see Table 1). The results show that the highest weighted human exposures resulted from metal cleaning operations, followed closely by commercial dry cleaners. Because these results are weighted by the number of people exposed to a particular level of atmospheric perc, they provide a useful basis for comparison. Assuming a linear dose response relationship, these weighted exposures are directly related to the expected risk to human health.

These preliminary estimates indicate that the number of people exposed is substantial. Further monitoring and sampling data are required for a more thorough and accurate assessment. Potential health effects of exposure to perc at environmental concentrations will be addressed in a separate report being prepared by the EPA Cancer Assessment Group.

Table 1

SUMMARY OF ESTIMATED POPULATION EXPOSURES TO ATMOSPHERIC PERC

Source	Number of People Exposed to Perc Concentrations (ppb) *					Comparison Among Sources†
	8-Hour Worst-Case Annual Average	0.25 - 1.3 0.01 - 0.05	1.4 - 2.5 0.06 - 0.10	2.6 - 25.0 0.11 - 1.00	25.1 - 100.0 1.01 - 4.00	TOTAL†	(10^6 ppb-persons-yrs)
Production Facilities	300,000	20,000	5,000	-	300,000	0.01
Dry Cleaning:						
Commercial	‡	20,000,000	11,000,000	41,000	30,000,000	7.8
Coin-operated	‡	2,600,000	790,000	-	3,000,000	0.6
Industrial	‡	2,900,000	1,800,000	4,000	5,000,000	1.2
Metal Cleaning	‡	20,000,000	11,000,000	120,000	30,000,000	8.0

---

* To convert to $\mu g/m^3$, multiply each exposure level by 6.7. A dash (-) signifies that no exposed population was estimated by our method for the annual average concentrations listed. There may be some people exposed to those concentrations for shorter periods of time. In addition, the analysis for dry cleaning and metal cleaning operations assumed that no people lived within certain distances of the plant.

† Totals are rounded to one significant figure. Population estimates are not additive vertically because double-counting exists, due to overlap of sources.

‡ Not estimated, because the closeness of the sources resulted in double-counting of the exposed population.

Source: SRI estimates.

II PERCHLORETHYLENE IN THE ENVIRONMENT

A. Introduction

Perchloroethylene (C_2Cl_4) is one of a number of chlorinated hydrocarbon solvents that have come under investigation by the federal government. The National Cancer Institute (NCI) has recently determined that perc causes cancer in mice when it is administered orally. The National Institute of Occupational Safety and Health (NIOSH) has urged industry to consider perc a human carcinogen as well. Currently, the Occupational Safety and Health Administration (OSHA) has set an exposure limit of 100 parts per million (ppm) for perc concentrations in the workplace. This limit may be revised downward as a result of the recent findings of NCI. The Consumer Product Safety Commission has provisionally proposed to classify perc as a Class A carcinogen, a procedure that is the first step in restricting the use of perc in consumer products. The outcome of the various proposed actions affecting perc could have a significant effect on its future use as a solvent.

The primary objective of this study has been to estimate the atmospheric exposure of the U.S. population to perc from each major source. This exposure information together with the health effects document being prepared by the U.S. Environmental Protection Agency Office of Research and Development will provide the necessary data for EPA's Cancer Assessment Group to make a determination of risk.

Because few quantitative data were available, all estimates given here are subject to considerable uncertainty. This uncertainty is related to: quantity of perc emissions, locations of emission sources, estimates of perc production and consumption, control technology employed, deterioration of control technology over time, and dispersion modeling. Insufficient atmospheric monitoring data are available to assess the accuracy of the modeling results. Comparisons of short-term ambient concentrations established by monitoring with annual average ambient concentrations estimated from dispersion modeling are tenuous. In addition, meteorological conditions and operating characteristics of facilities may be significantly different from the average. Despite these uncertainties, a comparison of monitoring data with dispersion modeling results suggests that the agreement between the two is sufficient to support the accuracy of the modeled concentrations.

B. Chemical and Physical Properties of Perchloroethylene

Perchloroethylene is a colorless, extremely stable, and nonflammable liquid with an ether-like odor. It is insoluble in water but miscible with alcohol, ether, and oils in all proportions. Perc has a relatively high density and a moderate boiling point and heat of vaporization. Pertinent physical properties are listed in Table 2.

Few reactivity studies of perc have been conducted. Huybrechts et al. (1967) studied the photochlorination and oxidation of perc under specialized conditions at 80 and 100°C. Analysis of the products in the completed experiments showed that 85 ± 5% of the oxidized perc appears as trichloroacetyl chloride and 15 ± 5% as phosgene. Trace quantities of carbon tetrachloride and tetrachloroethylene oxide were also detected. Studies to determine the rate constant for photochlorination of perc have been made by Horowitz et al. (1968), Goldfinger et al. (1961), and Dusoleil et al. (1961).

In 1976, Rutgers University (Appleby, 1976) completed an evaluation of the atmospheric fates of perc in a polluted atmosphere. In each system investigated, perc was chemically reactive under the influence of the light source used. The time needed to achieve a given level of decomposition varied significantly. The major decomposition products of perc included: phosgene, carbon tetrachloride, trichoracetyl chloride, and trichloroacetaldehyde. On the average, perc photodecomposition was found to cause the formation by weight of about 8% carbon tetrachloride and 70 - 85% phosgene in 7 days. Phosgene is a highly toxic material

Table 2

PHYSICAL PROPERTIES OF PERCHLOROETHYLENE

Properties	Value
Density, lb/gal*	13.55
Boiling point, °C**	121.0
Heat of vaporization, Btu/lb*	90.0
Flashpoint*	none
Freezing point, °C**	-22.4
Specific gravity @ 20°C**	1.625
Refractive index @ 25°C**	1.5029
Color*	water-white

---

*Fisher, 1977
**Hawley, 1977

with a threshold limit value (T.L.V.) of 0.05 ppm. A half-life of 2 days for photodecomposition of unstabilized perc has been reported in the literature (Lapp et al., 1977).

Fuller (1976) reported that perc reacts rapidly with hydroxyl ions (half-life of 8 days) and slowly with alkyl peroxy radicals and ozone (half-lives of 220 days and 11 years, respectively). Fuller found that perc decomposed to a mixture of phosgene and trichloroacetyl chloride in the presence of ozone.

Perc is corrosive to metals in the absence of chemical stabilizers such as organic amines. Below 140°C, stabilized perc is inert to air, water, light, and common construction metals (Franklin Institute Research Laboratories, 1975). In the absence of moisture, oxygen, and catalysts, the compound is stable to about 500°C. At 700°C, it decomposes on contact with active carbon to yield hexachloroethane and hexachlorobenzene.

The decomposition rates for perc in aerated water both in the presence of sunlight and in darkness were determined by Dillings et al. (1975). The half-life for the reaction in darkness was 8.8 months, whereas the half-life for the reaction in sunlight was only 6 months. The researchers believed that degradation was probably caused by oxidation and was probably free radical in nature. Dillings et al. also found that unstabilized perc decomposes to trichloroacetic and hydrochloric acids after contact with water for long periods at elevated temperature, and that perc is relatively resistant to hydrolysis. Because of its high vapor pressure and low solubility, perc will be rapidly removed by volatilization from agitated natural bodies of water (Dillings et al., 1975).

C. Sources of Perchloroethylene

The dry cleaning industry is the major user of perc, as Table 3 shows. The compound is also used in metal cleaning as a chemical intermediate for the production of C_2 fluorocarbons, in textile

Table 3

ESTIMATED CONSUMPTION OF PERC BY TYPE OF USE, 1978

Type of Use	Consumption* (10^6 Kg)	Percent of Total
Dry cleaning	160	53
Metal cleaning	50	17
Chemical intermediate	40	13
Textile processing	20	7
Miscellaneous**	30	10
Totals	300	100

---

*Rounded to the nearest ten.

**Includes product going into inventory.

Source: SRI estimates

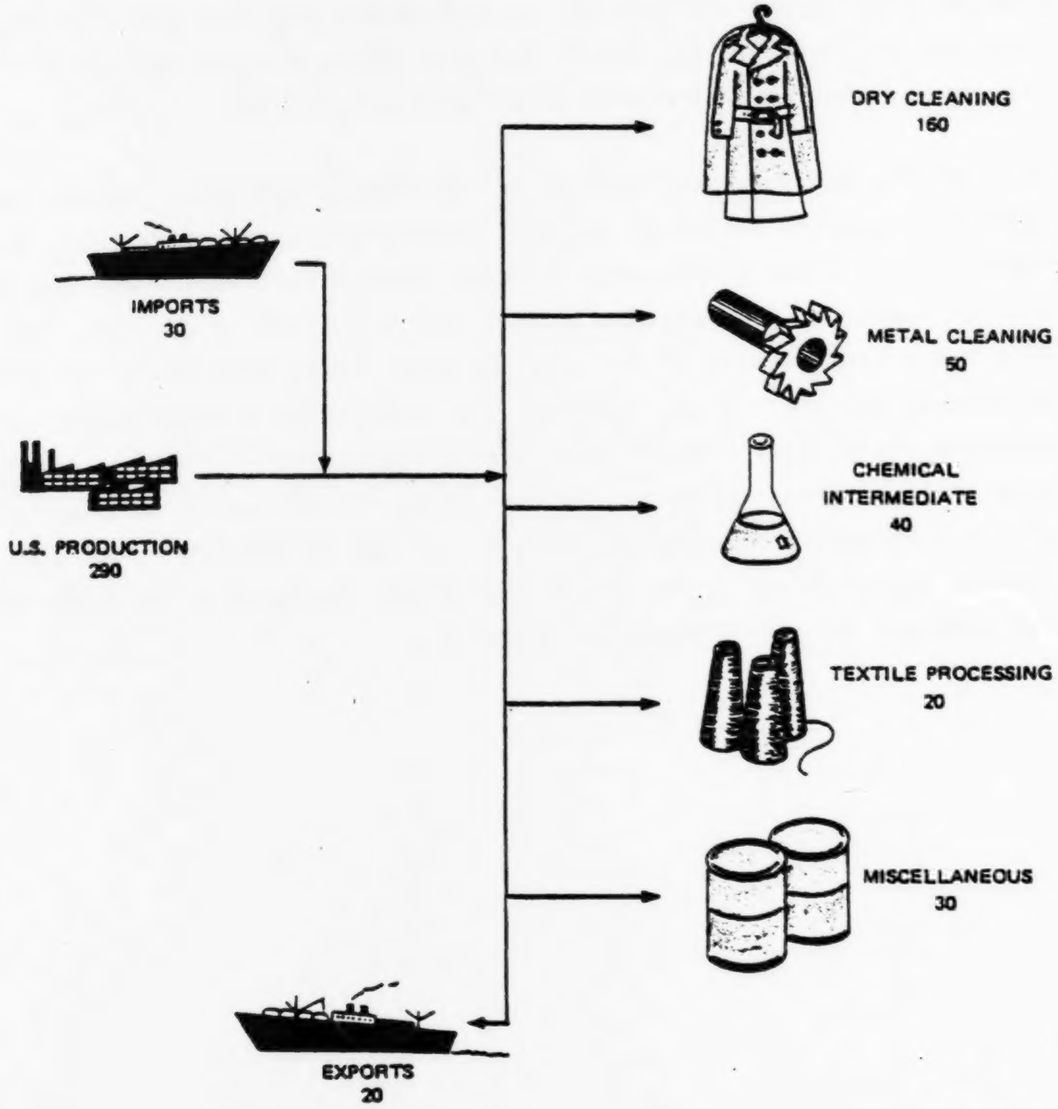
processing, and for miscellaneous purposes (e.g., as a solvent for silicones and as a constituent in aerosol specialty products for the laundry pretreatment market). The market distribution of perc is presented in Figure 1. Note that imports and exports of perc nearly balance and that U.S. production accounts for more than 90% of U.S. consumption.

Domestic consumption of perc in 1977 was about the same as it was in 1972, but it was 7% less than the peak reached in 1974. Growth to 1982 is expected to be small—probably less than 1.0% annually (SRI estimates).

In this report, three sources of perc emissions are evaluated: production facilities, dry cleaning operations, and metal cleaning operations. The analysis of production facilities includes those in which perc is used as a chemical intermediate. Consequently, our analysis covers all perc production (290 x 10^6 kg per year) and 83% of perc consumption (250 x 10^6 kg per year).

Exposures from textile processing facilities are not considered in our analysis. Although textile processing accounts for 7% of perc consumption, no information is available that would permit us to determine which facilities actually use perc. A quick survey of applicable Standard Industrial Classification (SIC) codes from the 1970 Census of Business showed that more than 2,500 facilities are engaged in textile processing operations that might involve the use of perc. The size of the group means that each facility probably uses only a small amount of perc and would emit a similarly small amount of perc to the atmosphere.

Perc is a manmade substance that is not released from any natural sources. It is not sampled regularly in any continuing air quality monitoring program. A few ambient measurements of perc have been made, and suggest that typical ambient concentrations are generally below 1.0 ppb. A report on atmospheric halogenated compounds prepared by Rutgers University (Appleby, 1976) summarized the measurements of perc available in the


IMPORTS
30
U.S. PRODUCTION
290
DRY CLEANING
160
METAL CLEANING
50
CHEMICAL
INTERMEDIATE
40
TEXTILE PROCESSING
20
MISCELLANEOUS
30
EXPORTS
20

Source: SRI estimates

FIGURE 1. MARKET DISTRIBUTION OF PERC, 1978 (10^6 kg)

214<

literature, as shown in Table 4. All measurements were 1.0 ppb or below. Rutgers also conducted a monitoring program in eight eastern U.S. cities. Their results are presented in Table 5. Note that New York City and Bayonne, New Jersey—both densely populated regions—had perc concentrations greater than 1.0 ppb and maximum concentrations near 10.0 ppb. On the other hand, Baltimore, Maryland, and Wilmington, Delaware--also densely populated regions—had mean perc concentrations less than 0.5 ppb.

The EPA Environmental Monitoring and Support Laboratory (draft report, 1979) has recently collected ambient measurements in New York City, Houston, and Detroit. These cities were selected because they were suspected to have a large number of perc sources in relation to population density. New York City has a large number of dry cleaning facilities, Houston has a perc production facility in the vicinity, and Detroit has a large number of metal cleaning operations. The 24-hour average concentrations of perc found at each sample station varied as follows: 0.16 - 10.61 ppb in New York City; <0.1 - 4.52 ppb in Houston, and <0.1 - 2.16 ppb in Detroit.* The high concentrations found in New York City probably result from emissions from dry cleaners and metal cleaning facilities.

---

* The detection level is 0.1 ppb for sampling techniques with easily replicable results.

Table 4

SUMMARY OF AMBIENT MONITORING DATA FOR PERC IN VARIOUS LOCATIONS

Source of Data	Location	Perc Concentration (ppb)
Kuriyang	Unknown	1.0
Williams	Unknown	1.0
Reid et al.	Unknown	1.0
Simmonds et al.	Los Angeles area	0.125
Lillian and Singh	New Brunswick	0.112

Source: Appleby, 1976

Table 5

AMBIENT CONCENTRATIONS OF PERC MEASURED BY RUTGERS UNIVERSITY, 1973-74

Location	Sampling Period (days)*	Concentration (ppb) Mean	Concentration (ppb) Maximum	Concentration (ppb) Minimum
Baltimore, MD	2	0.18	0.29	0.02
Bayonne, NJ	12	1.63	8.2	0.30
New York, NY	2	4.5	9.75	1.0
Sandy Hook, NJ	4	0.39	1.4	0.15
Seagirt, NJ	2	0.32	0.88	0.10
White Face Mountain, NY	4	0.07	0.19	0.02
Wilmington, DE	3	0.24	0.51	0.02
Wilmington, OH	4	0.15	0.69	0.02

---

* Discontinuous sampling for a few hours at a time.

Source: Appleby, 1976

III PRODUCTION FACILITIES

A. Source

Perc is produced at 10 facilities in 5 states: California, Kansas, Kentucky, Louisiana, and Texas. The company name and the location of each facility are shown in Table 6. The 1978 capacity for all facilities combined was 515 x 10^6 kg.* Actual production is estimated at 56% of the estimated U.S. production.

Perc is produced by three major processes. The most common process and one of the most economical is chlorination of C_1 to C_3 hydrocarbons or their partially chlorinated derivatives at high temperatures (500-540°C) with or without a catalyst. Propane is a common feedstock. Perc and carbon tetrachloride are both produced, and it is possible to vary the product distribution to produce more than 90% of either material. Large quantities of hydrochloric acid are produced by this process. The six production facilities that use this process account for 52% of the total estimated perc production.

Ethylene dichloride is used as the feedstock for two of the perc manufacturing processes. Perc is produced by high-temperature (400-450°C), noncatalytic chlorination of ethylene dichloride. Adjustments of the chlorine/ethylene dichloride ratio favor production of perc over trichloroethylene, which is also produced by this process. Large quantities of hydrochloric acid are produced. The three facilities that use this process account for 31% of the total estimated perc production.

---

*This figure does not include the capacity at the Hooker Chemical Corporation facility in Taft, Louisiana, which reportedly ceased production in March 1978.

Table 6

LOCATIONS OF AND PRODUCTION FIGURES FOR PERC FACILITIES

Location	Company*	Manufacturing Process**	1978 Capacity (10^6 kg)[†]	1978 Estimated Production (10^6 kg)[‡]
California				
Pittsburg	Dow Chemical USA	Cl-HC	20	10
Kansas				
Wichita	Vulcan Materials Co.	Cl-HC	20	10
Kentucky				
Louisville	Stauffer Chem. Co.	Cl-HC	30	20
Louisiana				
Baton Rouge	Ethyl Corporation	Cl-EDC	20	10
Geismar	Vulcan Materials Co.	Cl-HC	70	40
Lake Charles	PPG Industries, Inc.	Ox-EDC	90	50
Plaquemine	Dow Chemical USA	Cl-HC	50	30
Texas				
Corpus Christi	DuPont[§]	Cl-HC	70	40
Deer Park	Diamond Shamrock	Cl-EDC	75	40
Freeport	Dow Chemical USA	Cl-EDC	70	40
Total			515	290

---

*An August 1978 article in Chemical Marketing Reporter stated that the Hooker Chemical Corporation facility at Taft, Louisiana stopped producing perc in March 1978.

[†] Key to symbols: Cl-HC = Chlorination of C_1 to C_3 hydrocarbons or their partially chlorinated derivatives; Cl-EDC = chlorination of ethylene dichloride; Ox-EDC = oxychlorination of ethylene dichloride.

[‡] SRI estimates.

[§] Captive use only.

219<

Oxychlorination of ethylene dichloride is used to produce perc at one facility. In this process, which accounts for 17% of estimated production, perc and trichloroethylene may be produced either separately or as a mixture in varying proportions by reacting ethylene dichloride (or other C_2 chlorinated hydrocarbons) with a mixture of oxygen and chlorine or hydrochloric acid at about $430^{\circ}C$ over a suitable catalyst. This process avoids net production of hydrochloric acid and provides an outlet for unwanted hydrochloric acid from other processes.

Approximately 13% of the perc produced is consumed as a chemical intermediate in the formulation of a series of C_2 fluorocarbons: F-113, trichlorotrifluoroethane; F-114, dichlorotetrafluoroethane; F-115, chloropentafluoroethane; and F-116, hexafluoroethane. All the perc produced at the DuPont facility at Corpus Christi is used captively in the production of fluorocarbons from perc -- primarily F-113. Of the four fluorocarbons, F-113, which is used primarily as a premium solvent, is produced in the largest volume. F-113 is the basis for DuPont's Valclene® dry cleaning agent and is used as a cleaning solvent for special applications such as electronics and aerospace equipment. F-113 is also used to make chlorotrifluoroethylene, a monomer for fluorocarbon resins. Despite the high cost of F-113, use of it is expected to increase because of its low toxicity and its usefulness in special applications. F-114 is the second most important fluorocarbon derived from perc, but the volume of F-114 combined with that of the smaller members of the group is no more than half that of F-113.

Midwest Research Institute (MRI) conducted a survey in 1977 of the waste disposal practices of producers of chlorinated solvents for the EPA Office of Toxic Substances. The survey results are discussed in a draft final report (Lapp et al., 1977) that will soon be released in final form. The principal wastes from perc production are tarry residues ("hex" wastes) that contain hexachlorobenzene, hexachlorobutadiene, hexachloroethane, and other chlorinated compounds. Industry practices for disposal of these wastes vary, but generally include incineration and landfill. Table 7 summarizes the relevant information derived from the MRI survey.

Table 7

SUMMARY OF WASTE DISPOSAL PRACTICES AT PERC PRODUCTION FACILITIES

Company	Location	Disposal of Wastes from Perc Production
Diamond Shamrock	Deer Park, TX	Shipping in sealed containers to private company for incineration
Ethyl Corporation	Baton Rouge, LA	Deep-well disposal
PPG Industries	Lake Charles, LA	Incineration that operates at 1,371° C and uses aqueous scrubbers for HCl recovery and alkaline scrubbers for chlorine destruction.
Vulcan Materials	Wichita, KN	Incineration
	Geismar, LA	Impounded in a landfill

Source: Lapp et al., 1977

221<

Only one report on measurements of perc in the vicinity of production facilities has been found. Battelle (1977) sampled ambient concentrations at several facilities manufacturing trichloroethyelene and methyl chloroform. Most of these facilities also produce perc, and therefore perc measurements were made in conjunction with the other sampling. The pertinent results are shown in Table 8. All measurements were taken within 4 km of the facility, most were taken within 2 km.

B. Methodology

Because of the scope of this study detailed dispersion calculations that incorporate individual site meteorology are impractical. A simple method of assessment was therefore developed to permit comparative analysis. Variations in pollution control technology, physical surroundings, and meteorological conditions were not considered in the analysis. Because of these assumptions, the results are not precise but do provide a reasonable estimate of atmospheric perc concentrations and associated exposed population.

To assess the ambient perc concentrations in the vicinity of production facilities, two factors must be estimated: perc emission rates at each location, and atmospheric dispersion in the vicinity of the facility. Emission rates are estimated by applying an emission factor to estimated total production at the facility. One of two rough emission factors was used, depending on the particular manufacturing process used at the facility:

- Direct chlorination process — 0.002 kg emitted/kg produced

- Oxychlorination process - 0.005 kg emitted/kg produced.

These factors were determined by EPA (Greer, personal communication, 1978) on the basis of several very limited studies of perc losses during production. They do, however, provide a reasonable estimate of emissions from each facility. The emission rate for each production facility is shown in Table 9. Twenty-four hour operation over 365 days was assumed.

Table 8

RESULTS OF MONITORING FOR PERC AT FACILITIES PRODUCING TRICHLOROETHYLENE AND METHYL CHLOROFORM

Company	Location	Type of Production*	Number of Samples	Perc Concentration (ppb)†		
				Max.	Min.	Mean
Dow Chemical	Freeport, TX	MC	86	ND**	ND	ND
	Freeport, TX	TCE	51	3.4	0.3	0.5
Ethyl Corp.	Baton Rouge, LA	TCE	49	37.0	0.3	1.6
PPG Industries	Lake Charles, LA	MC,TCE	47	5.0	0.3	0.7
Vulcan Materials	Geismar, LA	MC	66	23.0	0.3	2.2

---

*I.e., the chemical produced at the particular facility sampled. Perc is also produced at each location, but the facilities may be separate. Information on the perc production facilities at each location was not available from this study. MC = methyl chloroform; TCE = trichloroethylene.

† Limit of detection was reported to be 0.3 ppb. To convert to $\mu g/m^3$, multiply by 6.7.

**ND = not determined.

Source: Battelle, 1977

Table 9

ESTIMATED EMISSIONS FROM PERC FACILITIES

Location	Company	Estimated Annual Emissions (10^3 kg)	Estimated Emission Rate (g/s)
California			
Pittsburg	Dow Chemical USA	20	0.63
Kansas			
Wichita	Vulcan Material Co.	20	0.63
Kentucky			
Louisville	Stauffer Chemical Co.	40	1.30
Louisiana			
Baton Rouge	Ethyl Corporation	20	0.63
Geismar	Vulcan Materials Co.	80	2.50
Lake Charles	PPG Industries, Inc.	250	7.90
Plaquemine	Dow Chemical USA	60	1.90
Texas			
Corpus Christi	DuPont*	80	2.50
Deer Park	Diamond Shamrock	80	2.50
Freeport	Dow Chemical USA	80	2.50

---

* Captive use for C_2 fluorocarbons; emission factor is unchanged.

Source: SRI estimates

The ambient concentrations of perc present in the vicinity of production facilities are estimated based on an earlier application by Youngblood (1977; described in Mara and Lee, 1978). Dispersion curves developed in a study of benzene exposures were modified for application to perc emissions (refer to Mara and Lee, 1978). A single dispersion curve was developed by regression analysis to reasonably represent dispersion from three source categories: ground-level point source (effective stack height, 0 m); building source (effective stack height, 10 m); and elevated point source (effective stack height, 20 m). The meteorological conditions assumed were: wind speed, 4 m/s; stability class, neutral (Pasquill Gifford "D"). Exhaust gas temperature, which is important in determining near-source concentrations, was not considered. The general dispersion curve for perc is shown in Figure 2. This curve was used to estimate ambient perc concentrations for all source categories: production facilities, dry cleaning operations, and metal cleaning operations.

Equation (3.1) is used to estimate 8-hour worst-case concentrations:

$$C = 16.48\ E_a\ D^{-1.48}. \qquad (3.1)$$

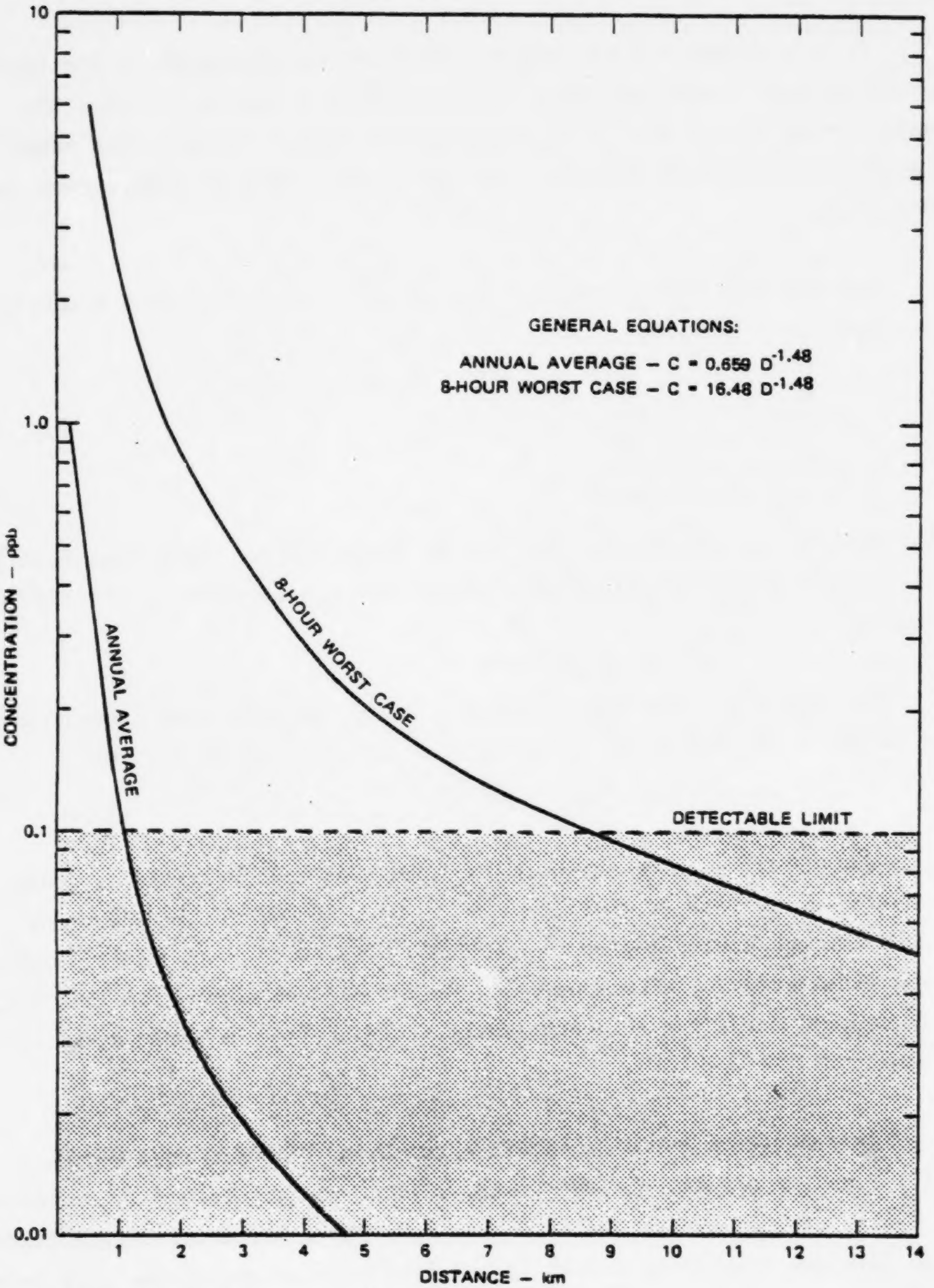
C is the 8-hour worst-case perc concentration in $\mu g/m^3$, E_a is the emission rate for the location of interest in g/s, and D is the distance from the source in km.

Annual average concentrations are estimated by including a multiplier of 0.04 in the equation. The equation, thus becomes:

$$C = 0.659\ E_a\ D^{-1.48}. \qquad (3.2)$$

This 0.04 conversion is based on results from previous studies. It represents the ratio of 8-hour concentrations to directionally-averaged annual concentrations. This conversion gives reasonable concentration estimates in keeping with the general nature of this study.

225<



Source: SRI estimates

FIGURE 2. GENERAL DISPERSION CURVE FOR PERC BASED ON AN EMISSION RATE OF 1.0 GRAM PER SECOND

226<

In this study, all population exposures are estimated on the basis of annual average concentrations. This approach is consistent with the requirements of a linear dose response model which assumes that exposures to higher concentrations for short periods of time have no higher risk associated with them.

For the sake of uniformity, the following ranges of perc concentrations were used in this study:

- 0.01 - 0.05 ppb
- 0.06 - 0.10 ppb
- 0.11 - 1.00 ppb
- 1.01 - 4.00 ppb.

All exposure estimates were confined to these ranges. Note that 0.10 ppb is the present limit for detection of perc that produces easily replicable results.

For each facility, the distance at which the specified concentrations are found is determined by rearranging equation (3.2) as follows:

$$D_i = 0.754 \left(\frac{Ea}{C_i} \right)^{0.6757} \qquad (3.3)$$

D_i is the distance in km at which the specified concentration is found; Ea is the emission rate at that location in g/s; and C_i is the specified annual average concentration (i.e., 0.01, 0.05, 0.10, 1.0, and 4.0 ppb; input data, however, are in $\mu g/m^3$). Emissions from production facilities were assumed to be the only contributors of perc to the atmosphere in the vicinity of the facility.

The population residing within a circle of radius D_i was estimated by SRI's computer system, BESTPOP (Suta, 1978). The population file consists of a grid of 1-km-square sections that span the continental United States. This file was created by assigning the 1970 populations to the grid network and by assuming uniform distribution of population within the 256,000 enumeration districts in the 1970 census. The computer software accesses the population file and accumulates residential population within specified radial rings about any given point. In addition, a rectangular map for and area around each specified point is printed out, and it shows the population by square kilometer.

The latitude and longitude of each facility was determined according to information provided by the company itself or from other studies completed for EPA. These data are shown in Table 10.

C. Exposures

Estimates of population exposed to perc emissions from production facilities are shown in Table 11. Approximately 5,000 people are exposed to perc at annual average concentrations greater than 0.1 ppb. Louisiana and Texas have the largest exposed populations. Exposures are relatively low level for two reasons: (1) perc emission rates are low; (2) facilities are usually located in sparsely populated areas. Consequently, few people are estimated to be exposed to perc from production facilities at concentrations higher than the detectable limit of 0.1 ppb.

Table 10

LOCATIONS OF EACH PERC PRODUCTION FACILITY BY LATITUDE AND LONGITUDE
(Degrees, Minutes, Seconds)

Company	Location	Source of Information*	Latitude	Longitude
Diamond Shamrock	Deer Park, TX	1	29.43.34	95.07.16
Dow Chemical	Pittsburg, CA	2	38.01.35	121.51.22
	Plaquemine, LA	1	30.19.15	91.14.56
	Freeport, TX	1	29.01.59	95.13.16
DuPont	Corpus Christi	3	27.52.30	97.15.00
Ethyl Corporation	Baton Rouge, LA	1	30.29.20	91.11.13
PPG Industries	Lake Charles, LA	1	30.12.36	93.17.06
Stauffer Chemical	Louisville, KY	3	38.12.30	85.52.30
Vulcan Materials	Wichita, KA	3	37.34.50	97.25.16
	Geismar, LA	1	30.10.23	90.57.58

---

*1 = EPA
2 = Association of Bay Area Governments, Berkeley, CA
3 = Company spokesmen

TABLE 11

POPULATION EXPOSED TO PERC FROM PRODUCTION FACILITIES

Location	Company	Population Exposed* to Perc (ppb)**			Total Exposed Population*
		0.01 - 0.05	0.06 - 0.10	0.11 - 1.00	
California					
Pittsburg	Dow Chemical Co.	20,000	500	-	20,000
Kansas					
Wichita	Vulcan Materials Co.	600	-	-	600
Kentucky					
Louisville	Stauffer Chemical Co.	40,000	-	-	40,000
Louisiana					
Baton Route	Ethyl Corporation	30,000	500	***	30,000
Geismar	Vulcan Materials Co.	10,000	-	-	10,000
Lake Charles	PPG Industries Inc.	100,000	20,000	5,000	100,000
Plaquemine	Dow Chemical USA	20,000	500	-	20,000
Texas					
Corpus Christi	DuPont	20,000	-	-	20,000
Deer Park	Diamond Shamrock	90,000	100	60	90,000
Freeport	Dow Chemical USA	1,000	-	-	1,000
Total Exposed Population*:		300,000	20,000	5,000	300,000

---

* Rounded to one significant figure.

** Annual average concentrations; to convert to 8-hour worst-case estimates, multiply by 25; to convert to $\mu g/m^3$, multiply by 6.7; a dash (-) signifies that our method estimated that no people were exposed at the annual average concentrations listed, although some people may be exposed at those concentrations for short periods of time.

*** Less than 10 people.

Source: SRI estimates.

Table 12

PERC CONSUMPTION BY TYPE OF DRY CLEANING OPERATION, 1978

Type of Operation	Number of Plants*	Percent Using Perc**	Number Using Perc[†]	Estimated Perc Consumption (10^6 kg)[‡]	Consumption as Percent of Total[†]
Commercial	22,000	74	16,000	123	77
Coin-operated	11,000	97[§]	11,000	23	14
Industrial	700	50	350	14	9
Total	33,700		27,350	160	100

---

*The number of coin-operated and industrial plants with dry cleaning equipment was estimated based on data from the Bureau of Census, 1974 County Business Patterns. The number of commercial cry cleaners was taken directly from that publication.

**Fisher, 1977.

[†] SRI estimates

[‡] Kleeberg, 1978.

[§] 3% use Fluorocarbon-113.

Business Patterns). However, only commercial dry cleaners have shown an actual decrease (down 15%) while coin-operated plants have increased by 17% and industrial plants have increased by 45%. (Note that some plants in the latter two categories are laundries with no dry cleaning equipment.)

2. Process Description

Dry cleaning is a three stage process. In the wash cycle, perc is passed through a rotating cylinder to remove soil from garments. The perc is continuously recirculated and usually passes through a diatomite or a cartridge filter for clarification. After the wash cycle, an extraction or centrifuging process is employed to remove as much perc as possible from the garments before they are dried. Extraction is usually carried out in the same cylinder that is used for washing. Perc that remains in the garments after extraction is removed in the drying cycle. Air is heated in a rotating cylinder and passed through the garments. The perc-laden air leaving the cylinder is passed over a water-cooled condenser to recover the perc. The same air is then reheated and recirculated in the recovery chamber. After an appropriate drying period, fresh air is drawn into the chamber and then exhausted to deodorize the garments. All three processes may be carried out in a single machine called a "hot unit", but it is more common to use a separate unit, called a recovery tumbler, for drying.

Filtration is not the only method used for clarifying perc. Periodic distillation at atmospheric pressure in either a still or a combination cooker/still with water separators is often used to recover perc. Because perc and water are immiscible, separators are usually simply small metal containers with baffles to facilitate the separation process.

The largest single loss of perc from dry cleaning plants that do not use carbon adsorption results from direct venting of solvent vapors to the atmosphere. An IFI survey (1975) of California dry cleaners estimated average losses at 20 gallons per plant per week.* Smaller amounts of perc also escape from solid residues, such as filter powder cookers and cartridge filters, and are lost in leaks and spills that occur during handling or at pipe joints. The average loss from solid waste has been estimated by IFI at 0.1 to 6 gallons per week per plant. Emissions associated with various dry cleaning processes and equipment are summarized in Table 13. The most common filtration system in commercial plants is a regenerative diatomite filter connected to a muck cooker (Fisher, 1977)

Most commercial dry cleaning establishments use separate dryers and transfer clothers manually. Clothes are sometimes transferred automatically in industrial plants, which decreases perc losses. Coin-operated cleaners always wash and dry in the same unit.

According to IFI, the relationship between the weight of the clothes cleaned and the capacity is the most significant factor affecting perc emissions. Fisher (1977) used that factor in estimating perc losses in California. His estimates, in pounds lost per California resident per year, are given in the following tabulation:

Total losses	
By reported perc consumption	1.99
By calculated perc consumption	2.26
Atmospheric losses	
By reported perc consumption	1.75
By calculated perc consumption	1.99

3. Emission Controls

Adequate control equipment can substantially reduce perc emissions. At present, the primary emission control techniques in dry cleaning plants are adsorption, filtration, distillation, condensation, and housekeeping. Vapor adsorbers (carbon sniffers) are the most sophisticated devices and are intended to remove all of the perc from the air before it is exhausted to the atmosphere outside the plant.

---

*No plant size was given in the report.

Table 13

PERC LOSSES FROM DRY CLEANING PROCESSES AND EQUIPMENT

Process	Average Perc Losses (kg lost/100 kg used)
Washer	0.5 - 1
Dryer	3 - 6
Filter	
- Diatomite (no cooker)	14
- Diatomite (with cooker)	1 - 1.6
- Cartridge	0.5 - 1.8
Still residue	1.6
Miscellaneous	1.2
Average total loss	12
- Range without vapor adsorber	8 - 21
- Range with vapor adsorber	3 - 18

Source: Fisher, 1977

235<

Data from a California survey (IFI, 1975) show that when washers and dryers are ducted to adsorbers emissions of perc from these two sources are effectively eliminated. However, exhaust air from about half of the cookers or stills is either vented into the processing room or piped outside the plant. Very high concentrations of perc are likely to occur at the outlets of such vents or pipes. Floor-level pick-ups for the adsorbers are often used to capture solvent vapors in the processing area (IFI, 1975).

Vapor adsorpers are estimated to be used in about 35% of commercial and industrial dry cleaning operations that use perc (Kleeberg, 1978). Adsorbers are rarely found in coin-operated dry cleaners. A recent survey of San Diego County (Evatovich, 1978) showed that 100% of the dry cleaners in the county have vapor condensers and 45% have vapor adsorbers. Data on adsorber efficiency and measurements of vapor concentrations in adsorber exhaust are given in Table 14. The San Diego survey showed that about two-thirds of the absorbers in dry cleaning plants were exhausting up to 40 times more perc vapor than manufacturer's specifications claimed they would (Evatovich, 1978).

4. Monitoring Data

Three studies of perc emissions from two types of dry cleaning operations have been conducted, and the results were summarized by Lapp et al. (1977). Midwest Research Institue (1976a) sampled a large industrial facility in San Antonio, Texas. The plant employs a 250-lb transfer system equipped with a single carbon adsorption bed. The vapor adsorber is used for only a part of each cleaning cycle; during other segments of the operation, the system is either sealed or vented directly to the atmosphere. Perc concentrations measured in the outlet air vent averaged 3 ppm for the first 2 days and 1 ppm for the third day of testing.

Midwest Research Institute (1976b) conducted a second study of a small, neighborhood commercial dry cleaning operation in Kalamazoo, Michigan. The facility used a 40-lb, dry-to-dry system with dual carbon adsorption beds. Average concentrations in samples from the outlet air vent

Table 14

PERC LOSSES FROM DRY CLEANING PLANTS WITH VAPOR ADSORBERS

Plant No.	Hours Used Per Day	Frequency of Stripping Vapor Adsorber Bed	No. Loads Per Week	Base Reading (ppm)	Maximum (ppm)	Perc Losses (Gal/Week)
1	6	Daily	75	500	900	26.8
5	8	1 Bed/day	109	200	--	13.5
10	8	Every 3 days	65	1,000	1,000	20.7
12	10	Weekly				
13	8	3 1/2 days	50	900	1,000	19.8
14	8		211 (70 per machine)	500	--	37.5
20	8	1 Bed/day	85	20	--	1.0
22	Every	Each load	60	NA	NA	1.3
24	8	Daily	35	240	No peak	12.2
27	8	Daily	270	70	No peak	3.4
29	8	Daily	30	10	No peak	0.5
30	8	Daily	80	10	No peak	0.5
31	8	1 Bed/load	35	10	No peak	0.5
34	Only when cleaning	Daily	40	700	No peak	15.8
35	8	Daily	45	30	No peak	1.7
43	8	Daily	110	NA	NA	150.8
44	Only when cleaning	Daily	40	220	No peak	4.0
45	8	1 Bed/day	145	700	No peak	38.1
48	8	1 Bed/day	75	NA	NA	

Source: IFI, 1975

ranged from 73 to 138 ppm. Table 15 gives an example of how emissions varied with the type of the load.

A third study sampled a fairly large commercial operation in Hershey, Pennsylvania (Scott, 1976). This facility used a 110-lb washer and two dryers with a dual carbon adsorption bed. Hourly average concentrations of perc in the outlet air vent pipe were measured for a 3-day period. The average perc concentration was 22.8 ppm and ranged from 5 to 72 ppm.

Results of occupational exposure monitoring indicate that machine operators are exposed at the highest average concentrations (see Table 16). The lowest exposure concentrations are experienced by the employees who work at the counter.

B. Methodology

A simple method of assessment similar to that described in Chapter III was developed for dry cleaning operations that allows a comparative analysis of exposures from various sources. Variations in pollution control technology, physical surroundings, meteorological conditions, and weight of the garments cleaned were not considered in the analysis.

Few studies have provided information on characteristics of the dry cleaning industry. As a result, little is known about the location of facilities, the extent to which dry cleaners are used by the local population, perc use per facility, the extent and effectiveness of emission controls, and the distribution of facilities within urban areas. Therefore a number of assumptions had to be made.

Exposures were projected only for cities with populations of 25,000 or more. Limiting the analysis in this way seems justifiable because the population density of smaller cities is usually much lower.

Little information exists that documents differences in the density of dry cleaners in various areas of the United Staes, although it is

Table 16

PERC EXPOSURE DATA FOR EMPLOYEES IN COMMERCIAL DRY CLEANING PLANTS

	Number of People Sampled	Mean Time-Weighted Average (ppm)	Mean Breathing Zone Sample (ppm)	Mean Peak (ppm)
Machine operator	5	37.2 (±24.96)	20.47 (±18.21)	214.90 (±179.41)
Presser	2	11.43 (±6.82)	4.48 (±0.39)	51.85 (±64.56)
Counter	5	1.32 (±0.97)	0.95 (±0.62)	2.61 (± 1.87)
Miscellaneous	7	3.03 (±2.09)	2.04 (±2.29)	27.45 (±46.02)

Source: Tuttle et al., 1977.

Table 17

DENSITY OF DRY CLEANERS IN SELECTED CITIES

Location	Number of Dry Cleaners	1970 Population	Density (Population/Dry Cleaner)
Michigan			
Detroit	265	1,355,000	5,113
Grand Rapids	51	197,649	3,875
Kalamazoo	25	85,661	3,426
Lansing	32	134,400	4,200
Colorado			
Denver	113	514,678	4,555

Source: Michigan Department of Public Health, 1977.

242<

7. No one resides within a circle of radius 200 m around small operations (less than 20 employees) and within a circle of radius 300 m around larger operations (more than 20 employees).

8. Urban density was uniform for all cities in a state. (Density was calculated by summing the population and the land area of cities in each state with more than 25,000 residents and dividing the former by the latter.)

The number of dry cleaners using perc was estimated on the basis of the data in Table 12. For our estimates, 75% of commercial dry cleaners were assumed to use perc. The data for coin-operated plants included laudromats without dry cleaning facilities. Our estimates assume that 75% of coin-operated plants have dry cleaning equipment and that all coin-operated dry cleaners use perc. Similarly, the data for industrial plants included plants without dry cleaning facilities. Our estimates assume that 75% of industrial plants have dry cleaning equipment and that 50% of the industrial dry cleaners use perc.

In addition, the number of dry cleaners in urban areas had to be estimated. Estimates of the number in urban areas were based on the ratio between the urban and the rural population in each state according to 1970 census data (Bureau of Census, 1972 County and City Data Book). This ratio was then applied to the total number of dry cleaners in the smaller size categories (less than 20 employees). All of the larger dry cleaners were assumed to be located in urban areas. For example, the State of Massachusetts has a ratio of 0.51 (i.e., 51% of the State's population resides in cities with a population greater than 25,000). The 1974 edition of County Business Patterns reports that Massachusetts has 171 commercial dry cleaners (SIC 7216) with 1-4 employees. We assumed that 51% of these would be in urban areas and that 75% of them use perc. Thus, we estimated that 65 commercial dry cleaners in the 1-4 size category are point sources of perc in Massachusetts. Six commercial dry cleaners have more than 50 employees. All were assumed to be located in urban areas, and 75% were assumed to use perc; thus, there were five point sources of perc in that size category in Massachusetts.

The estimated number of dry cleaners of all three types using perc in urban areas is shown in Table 18. A state-by-state breakdown is given in Appendix A.

Emission rates for each type of operation were determined on the basis of annual perc consumption. We assumed that all perc purchased in a given year was lost to the atmosphere. We then divided total perc consumption by the total number of employees for each type of dry cleaning operations. An emission rate per employee was estimated. The emission rates estimated for each type of dry cleaner are shown in Table 19.

Dispersion in the vicinity of each plant was determined from Figure 2 and Equation (3.3). A computer program was written to estimate the number of people exposed to perc in each state based on population and urban density data from the 1972 County and City Data Book, which is the most recent available aggregated data for cities larger than 25,000.

C. Exposures

Estimates of the population exposed to perc from dry cleaning operations are given in Table 20. More than 35% of the U.S. urban population is exposed to perc from commercial dry cleaners at concentrations greater than 0.05 ppb. The estimated population exposures are much lower for coin-operated and industrial dry cleaners. Both commercial and industrial dry cleaners caused exposures at concentrations greater than 1.0 ppb. A detailed breakdown of these data by state is given in Appendix A. Nine states — California, Illinois, Maryland, Michigan, New Jersey, New York, Ohio, Pennsylvania, Texas — accounted for more than 70% of the total exposures from each type of dry cleaning operation. New York had the largest exposures, acounting for 22% of all exposures from commercial dry cleaners, 26% of those from coin-operated dry cleaners, and 18% of those from industrial dry cleaners.

As previously discussed, very few data are available on U.S. dry cleaning operations. Changes in life styles and textile materials have

Table 18

ESTIMATED NUMBER OF URBAN DRY CLEANERS USING PERC BY SIZE OF OPERATION

Type of Operation	Numbers* of Operations By (Number of Employees)					
	1-4	5-9	10-19	20-49	50	Total*
Commercial	4.200	1,900	850	700	120	7,800
Coin-operated	3,700	500	120	60	10	4,400
Industrial	20	10	20	100	110	260

---

* Rounded to two significant figures.

Source: SRI estimates

Table 19

ESTIMATED EMISSION RATES FOR EACH TYPE OF DRY CLEANING OPERATION

		Emission Rates (g/s)				
	Size (employees)	1-4	5-9	10-19	20-49	50
Type of Operation	Average Number of Employees	2	6	14	35	70
Commercial		0.11	0.25	0.53	1.2	2.5
Coin-operated		0.072	0.17	0.36	0.84	1.7
Industrial		0.075	0.18	0.38	0.88	1.8

Source: SRI estimates

246<

Table 20

POPULATION EXPOSED TO PERC FROM DRY CLEANERS

Operation	Population Exposed* to Perc (ppb)** 0.06 - 0.10	 0.11 - 1.00	 1.10 - 4.00	Total* Exposed Population
Commercial	20,000,000	11,000,000	41,000	31,000,000
Coin-operated	2,600,000	790,000	—	3,400,000
Industrial	2,900,000	1,800,000	4,000	4,700,000

---

*Rounded to two significant figures; totals do not sum vertically because of double counting due to overlap of sources.

**Annual average concentration; to convert to 8-hour worst case, multiply by 25; to convert g/m^3, multiply by 6.7.

Source: SRI estimates

affected the industry in recent years. The exposure projections in this report have therefore been based on many assumptions and can only be considered approximations. The number of people who may be exposed is likely to slowly decrease if the number of dry cleaning plants operating in the United States continues its current decline. The addendum to this report contains a cursory assessment of the possible number of people exposed to perc while washing or dry cleaning clothes at coin-operated facilities.

V METAL CLEANING OPERATIONS

A. Sources

1. General

Metal cleaning can be divided into three major categories: cold cleaning, open-top vapor degreasing, and conveyorized degreasing. A cold cleaner is a tank of solvent, usually with a cover for nonuse periods. Inside this tank is a work surface or basket suspended over the solvent. An open-top vapor degreaser resembles a large cold cleaner. However, the solvent in it is heated to its boiling point, creating a zone of solvent vapor contained by a set of cooling coils. Both the cold cleaner and the open-top vapor degreaser are used to clean individual batches of parts at a time; thus, they are termed "batch loaded." A conveyorized degreaser is loaded continuously by means of various types of conveyor systems; it may operate as either a vapor degreaser or a cold cleaner (Office of Air Quality Planning and Standards, 1977).

The EPA Office of Air Quality Planning and Standards (OAQPS) (1977) estimates that 1,220,000 cold cleaning units were operating in the United States in 1974, about 70% of them devoted to maintenance and servicing operations and the remainder used in manufacturing operations. In the same year, an estimated 21,000 open top vapor degreasers and 3,700 vapor degreasers were operating. Projected growth in the degreasing industry is shown in Table 21. It is estimated that these degreasing operations used 726,000 metric tons of solvents of all types in 1974. Estimated 1974 consumption by solvent type is shown in Table 22. Estimated 1974 and 1975 consumption of halogenated degreasing solvents is shown in Table 23. The use of perchloroethylene decreased in cold cleaning operations and increased in vapor degreasing operations during this period. Perchloroethylene accounts for about 15% of the solvents used in vapor degreasing. Consumption of perchloroethylene in degreasing is estimated at 54,000 metric

249<

Table 21

PROJECTED GROWTH IN SOLVENT METAL CLEANING INDUSTRY, 1974-1985

Year	Cold Cleaners	Number of Open Top Vapor Degreasers	Number of Conveyorized Degreasers
1974	1,220,000	21,000	3,700
1975	1,250,000	24,000	3,900
1976	1,280,000	27,000	4,200
1977	1,310,000	29,000	4,400
1978	1,340,000	32,000	4,600
1979	1,380,000	35,000	4,900
1980	1,410,000	39,000	5,100
1981	1,450,000	42,000	5,400
1982	1,490,000	46,000	5,700
1983	1,530,000	50,000	6,000
1984	1,570,000	54,000	6,400
1985	1,620,000	58,000	6,700

Source: OAQPS (1977)

Table 21

PROJECTED GROWTH IN SOLVENT METAL CLEANING INDUSTRY, 1974-1985

Year	Cold Cleaners	Number of Open Top Vapor Degreasers	Number of Conveyorized Degreasers
1974	1,220,000	21,000	3,700
1975	1,250,000	24,000	3,900
1976	1,280,000	27,000	4,200
1977	1,310,000	29,000	4,400
1978	1,340,000	32,000	4,600
1979	1,380,000	35,000	4,900
1980	1,410,000	39,000	5,100
1981	1,450,000	42,000	5,400
1982	1,490,000	46,000	5,700
1983	1,530,000	50,000	6,000
1984	1,570,000	54,000	6,400
1985	1,620,000	58,000	6,700

Source: OAQPS (1977)

250<

Table 21

PROJECTED GROWTH IN SOLVENT METAL CLEANING INDUSTRY, 1974-1985

Year	Cold Cleaners	Number of Open Top Vapor Degreasers	Number of Conveyorized Degreasers
1974	1,220,000	21,000	3,700
1975	1,250,000	24,000	3,900
1976	1,280,000	27,000	4,200
1977	1,310,000	29,000	4,400
1978	1,340,000	32,000	4,600
1979	1,380,000	35,000	4,900
1980	1,410,000	39,000	5,100
1981	1,450,000	42,000	5,400
1982	1,490,000	46,000	5,700
1983	1,530,000	50,000	6,000
1984	1,570,000	54,000	6,400
1985	1,620,000	58,000	6,700

Source: OAQPS (1977)

Table 22

NATIONAL DEGREASING SOLVENT CONSUMPTION (1974)

	Solvent Consumption (10^3 metric tons)		
Solvent Type	Cold Cleaning	Vapor degreasing	All degreasing
Halogenated:			
Trichloroethylene	25	128	153
1,1,1 Trichloroethane	82	80	162
Perchloroethylene	13	41	54
Methylene Chloride	23	7	30
Trichlorotrifluoroethane	10	20	30
	153	276	429
Aliphatics	222		222
Aromatics:			
Benzene	7		
Toluene	14		
Xylene	12		
Cyclohexane	1		
Heavy Aromatics	12		
	46	0	46
Oxygenated:			
Ketones:			
Acetone	10		
Methyl Ethyl Ketone	8		
Alcohols:			
Butyl	5		
Ethers	6		
	29	0	29
Total Solvents:	450*	276 †	726

Source: OAQPS (1977)

* Includes 25,000 metric tons from conveyorized cold cleaning degreasers.

† Includes 75,000 metric tons from conveyorized vapor degreasers.

Table 23

U.S. HALOGENATED SOLVENT CONSUMPTION
BY TYPE OF DEGREASING OPERATION (1974 and 1975)

Solvent	Consumption, 10^3 Metric Tons			
	Cold Cleaning		Vapor Degreasing	
	1974	1975	1974	1975
Trichloroethylene	25	5.4	128	112
1,1,1-Trichloroethane	82	100	80	62
Perchloroethylene	13	4	41	45
Methylene chloride	23	0.4	7	9
Trichlorotrifluoroethane	10	NA	20	20

NA = Data not available.
Source: Mitre Corporation (1978)

tons in 1974 and 49,000 metric tons in 1975. Consumption in 1976 and 1977 is estimated to have remained stable at 50,000 metric tons. Future consumption of perchloroethylene in degreasing is difficult to estimate because possible regulations to reduce emissions and limit worker exposure to its vapors could affect it; however, SRI believes that its use as a degreaser will remain stable or will increase at no more than 2% annually. At this rate of increase, 50,000 - 55,000 metric tons would be used in 1982.

2. Service/Maintenance Industry Degreasing

Solvent degreasing is used in both the service/maintenance and manufacturing industries. The primary solvent degreasing users in the service/maintenance industry include service stations, automotive repair shops, oil well operations, maintenance for railroads, and maintenance for civilian and military aircrafts.

The automotive repair industry includes service stations, car and truck dealers, general and specialized auto maintenance shops, and small engine repair facilities. The solvents used in these shops are almost exclusively of the Stoddard or mineral spirits type, and they are used at room or slightly higher temperatures (Leung et al., 1978a).

Oil wells also require periodic maintenance, including organic solvent degreasing. For obvious reasons, petroleum products are widely used for degreasing in this industry (Leung et al., 1978a).

The railroad industry follows a schedule of routine maintenance to assure adequate vehicle performance. Locomotives must be cleaned and degreased regularly to facilitate inspection and maintenance. According to the Eureka survey of California railroads (Leung et al., 1978a), the majority of maintenance cleaning is done with alkaline cleaners. Relatively small amounts of chlorinated solvents (including perchloroethylene) are used primarily in cleaning electrical parts such as generators. Heavy maintenance may involve a more extensive use of chlorinated solvents; for Southern Pacific's Sacramento heavy maintenance, the solvent was 1,1,1-trichloroethane.

Civilian and military aircraft require periodic scheduled maintenance to assure continuous safe performance. Degreasing is an important aspect of the maintenance. The Eureka survey (Leung et al., 1978a) found no perchloroethylene used on military aircraft in California. The Eureka survey of civilian aircraft maintenance was less comprehensive. It found that one large commercial airline uses several vapor degreasers, but the type of solvent was not reported. The survey also found that two small airports servicing private aircraft use Shell or Chevron solvent. The formulations were not specified.

3. Manufacturing Industry Degreasing

The metal-working industry is the major user of solvent metal cleaning. These industry categories are included in eight (2-digit) SIC codes (25 and 33-39). Examples of industries in these classifications are automotive, electronics, appliances, furniture, jewelry, plumbing, aircraft, refrigeration, business machinery, and fasteners. In all of these industries, organic solvents are frequently used for metal cleaning. However, solvents are also used for metal cleaning in non-metal working industries such as printing, chemicals, plastics, rubber, textiles, glass, paper, and electric power. In these industries, organic solvents are usually used for maintenance cleaning of electric motors, fork lift trucks, printing presses, and other kinds of equipment (OAQPS, 1977).

The Eureka survey (Leung et al. 1978a) collected data on the degreasing solvents used in industries covered by 45 industrial 3-digit SIC codes in the state of California. These SIC codes are listed in Table 24. Questionnaires were sent to 1,505 randomly selected manufacturers, or about 10.3% of the 14,404 appropriate California manufacturers. Responses were received from about 841 companies for a survey response of 56%. Approximately one-third of these manufacturers used an organic solvent for degreasing.

SRI obtained the work sheets for this survey (Leung et al., 1978b) and subsequently analyzed them to determine perchloroethylene use in industrial degreasing. Manufacturers in 17 of the 45 SICs surveyed used

Table 24

CATEGORIES OF MANUFACTURERS USING DEGREASING SOLVENTS

SIC Code	Subcategory of Manufacturer
25	Furniture and Fixtures
251	Household Furniture
252	Office Furniture
253	Public Building & Related Furniture
254	Partitions and Fixtures
259	Miscellaneous Furniture and Fixtures
33	Primary Metal Industries
331	Blast Furnace and Basic Steel Products
332	Iron and Steel Foundries
333	Primary Nonferrous Metals
334	Secondary Nonferrous Metals
335	Nonferrous Rolling and Drawing
336	Nonferrous Foundries
339	Miscellaneous Primary Metal Products
34	Fabricated Metal Products
341	Metal Cans and Shipping Containers
342	Cutlery, Hand Tools, and Hardware
343	Plumbing and Heating, Except Electric
344	Fabricated Structural Metal Products
345	Screw Machine Products, Bolts, etc.
346	Metal Forgings and Stampings
347	Metal Services
348	Ordnance and Accessories
349	Misc. Fabricated Metal Products
35	Machinery, Except Electrical
351	Engines and Turbines
352	Farm and Garden Machinery
353	Construction and Related Machinery
354	Metalworking Machinery
355	Special Industry Machinery
356	General Industrial Machinery
357	Office and Computing Machines
358	Refrigeration and Service Machinery
359	Misc. Machinery, except Electrical
36	Electric and Electronic Equipment
361	Electric Distributing Equipment
362	Electrical Industrial Apparatus
363	Household Appliances
364	Electric Lighting and Wiring Equipment
365	Radio and TV Receiving Equipment
366	Communication Equipment
367	Electronic Components and Accessories
369	Misc. Electrical Equipment & Supplies
37	Transporation Equipment
371	Motor Vehicles and Equipment
372	Aircraft and Parts
373	Ship and Boat Building and Repairing
376	Guided Missiles, Space Vehicles, parts
379	Miscellaneous Transportation Equipment
38	Instruments and Related Products
381	Engineering and Scientific Instruments
382	Measuring and Controlling Devices

Source: Leung et al. (1978a).

perc. The fraction of the manufacturers in these SIC codes that use perc and their estimated annual consumption are given in Table 25.

B. Methodology

1. Emissions-Cold Cleaners

Emissions from cold cleaning occur during: (1) bath evaporation, (2) solvent carry-out; (3) agitation; (4) waste solvent evaporation; and (5) spray evaporation. The emission rates vary widely by operation. On the basis of national consumption data, OAQPS (1977) calculated an average national emission rate for all degreasing solvents of 0.3 metric ton per unit per year. OAQPS (1977) estimated that cold cleaners used for maintenance and manufacturing emit approximately 0.25 and 0.5 metric tons per year, respectively. Data from Safety Kleen Corporation show that only 0.17 metric tons are emitted for their cold cleaners each year. However, emissions from Safety Kleen's operations are expected to be lower than those of others because most of Safety Kleen's waste solvent is distilled and recycled by the company.

2. Emissions-Open-Top Vapor Degreasers

Unlike cold cleaners, open-top vapor degreasers lose a relatively small proportion of their solvent in the waste material and as liquid carry-out. Rather, most of their emissions are the vapors that diffuse out of the degreaser. Open-top vapor degreasing emissions, like those from cold cleaners, vary widely, depending on the operation. OAQPS (1977) estimates that an average open-top vapor degreaser emits about 2.5 kg per hour per m^2 of surface area at the opening. These estimates are derived from national consumption data on vapor degreasing solvents and from seven EPA tests. Assuming that an average open-top vapor degreaser would have an open-top area of about 1.67 m^2, a typical emission rate would be 1.2 g/s.

3. Emissions-Conveyorized Degreasing

Conveyorized degreasers may be of several types and may operate with either cold or vaporized solvents. About 85% of the conveyorized degreasers are vapor types, and 15% are nonboiling degreasers (OAQPS, 1977). Most of the nonboiling conveyorized degreasers are board cleaners.

Table 25

ESTIMATED PERCHLOROETHYLENE USED FOR DEGREASING IN THE MANUFACTURING INDUSTRY

SIC Code[*]	Fraction Using Perc Number of Employees 0-20	 >20	Amount of Perc Used per Plant (gal/yr) Number of Employees 0-20	 20-100	 >100
331	0.00	0.11	—	1,800[†]	10,000
336	0.00	0.06	—	45[†]	250
339	0.00	0.14	—	12,000	67,200[†]
342	0.00	0.09	—	2,655[†]	14,752
343	0.00	0.14	—	2,750	15,400[†]
344	0.00	0.08	—	350	1,960[†]
345	0.00	0.18	—	863[†]	4,795
347	0.08	0.11	330	5,262	17,044[†]
349	0.00	0.14	—	1,310	7,336[†]
352	0.00	0.11	—	90[†]	500
361	0.00	0.07	—	149[†]	825
362	0.17	0.00	219	—	—
364	0.00	0.07	—	73[†]	403
366	0.00	0.11	—	176[†]	980
367	0.06	0.00	700	—	—
371	0.00	0.05	—	110	616[†]
372	0.10	0.22	10	490	25,703

---

[*] Industries covered by SIC codes not listed are estimated not to use perchloroethylene in degreasing.

[†] These amounts have been extrapolated on the basis of the number of employees in the plant.

Source: Based on data from Leung et al. (1978b)

The average emission rate from a conveyorized vapor degreaser is about 25 metric tons per year (0.8 g/s), whereas the average for nonboiling conveyorized degreasers is almost 50 metric tons per year (1.6 g/s). However, more recent designs for nonboiling conveyorized degreasers are far more efficient than older designs. It is estimated that the vapor degreaser currently contribute about 75% of the conveyorized degreaser emissions in the United States. Nonboiling types contribute the remaining 25% (OAQPS, 1977). It is also estimated that 75,000 metric tons were emitted from conveyorized nonboiling degreasers (OAQPS, 1977). Evaporation, carry-out emissions, and exhaust emissions are the primary sources.

4. Perchloroethylene emissions

The Mitre Corporation (Mitre, 1978) estimates that more than 98% of the perc purchased annually for degreasing is emitted to the environment. During 1975, more than 90% of the perc was used in vapor degreasing (Table 23). OAQPS (1977) estimates that only 10-20% of the virgin solvent from conveyorized vapor degreasers, and 20-25% of the virgin solvent from open-top vapor degreasers, is disposed of as waste solvent. Most conveyorized vapor degreasers distill and recycle their own solvent. Used solvents from open-top degreasers are usually transferred to another system or company for distillation. The preferable methods for minimizing waste solvent evaporation into the atmosphere are distillation plants and special incineration plants. Disposal in landfills after evaporation is also used, but this is a less desirable method. Current waste disposal practices are such that most of the waste can evaporate into the atmosphere. A large fraction of perc waste is indiscriminately dumped into drains or onto the grounds surrounding the facilities that used it. Some waste solvent is stored in open containers; it evaporates. A small amount of waste solvent finds its way to municpal or chemical landfill where little attempt is made to encapsulate it (OAQPS, 1977).

5. Exposure Estimates

The results of the Eureka survey show that almost all the perc used for metal cleaning is consumed by manufacturing industries. Consequently, the population exposure estimates given in this report cover only emissions from manufacturing industries. An analysis of the Eureka survey data has provided estimates of the fraction of manufacturers of a particular type (SIC) that use perc for degreasing and has also provided estimates of the amount of perc purchased by these users. These data, categorized by manufacturer size (<20, 20-100, and >100 employees) for the industries that use perc were summarized in Table 25.

Data on the number of manufacturers in each state categorized by SIC code and by plant size, have been obtained from the 1976 Bureau of Census report on 1974 County Business Patterns. These data are too lengthy to be included in this report; however, the national totals are summarized in Table 26. The number of manufacturers that use perc for metal cleaning was estimated by multiplying the number of such manufacturers by the fraction that used perc in the Eureka survey (Table 25). This procedure resulted in an estimate of the number of plants in each state (by plant size and SIC) that use perc. Table 25 also provides an estimate of the amount of perc purchased annually for each of these plants. All of these data were used to project the national consumption for metal cleaning in manufacturing. This approach yielded an estimate of annual perc consumption of 43,000 metric tons. Independent estimates indicate that 49,000 metric tons of perc is purchased annually for all metal cleaning (Table 23), so the national industrial manufacturing projections based on the Eureka, California survey are remarkably accurate. Some perc is undoubtedly used in nonmanufacturing industries, which would account for some of the difference. In estimating atmospheric exposures, it must be remembered that approximately 10-20% of the perc is eventually disposed of as waste and that less than 100% of the perc in the waste enters the atmosphere causing human exposures. Therefore, although the projections of perc use based on the Eureka survey slightly underestimate the perc used for all degreasing, they are assumed to be a close approximation of the amount of perc being emitted to the atmosphere as a result of metal cleaning in industrial manufacturing.

To facilitate exposure calculations, each manufacturing plant thought to use perc for degreasing was assigned to 1 of 13 use groupings based on the amount of perc purchased annually. These 13 use groupings are given in

259<

Table 26

FACILITIES OF SELECTED SIC CODES* AND SIZES IN THE UNITED STATES

SIC	Number of Employees		
Code	< 20	20-100	> 100
331	2,795	2,322	1,868
336	923	614	230
339	590	389	52
342	956	506	360
343	363	183	166
344	6,026	3,221	938
345	1,388	853	240
347	3,245	1,203	117
349	2,652	1,619	641
352	906	511	281
361	275	151	138
362	674	405	398
364	877	594	399
366	869	582	500
367	1,397	903	693
371	1,776	883	752
372	467	311	270

---

* These are the industries that were found by the Eureka survey to use perc.

Source: 1974 County Business Patterns

given in Table 27, which also lists estimates of perc emissions (g/s) and of the number of U.S. plants in each use grouping. The number of plants in each use grouping was actually calculated on a state-by-state basis for estimating population exposures.

Dispersion modeling was used to estimate annual average atmospheric perc concentrations as a function of distance from manufacturing plants for each of the 13 perc use groupings. The dispersion model has previously been described (refer to Chapter III; Figure 2), and involves the use of the Equation (3.3). Because it was assumed that no one resides within 0.5 km of any of the manufacturing facilities, exposure concentrations at distance of less than 0.5 km from a plant were not estimated. With this exclusion, it was estimated that no population was exposed at concentrations greater than 4 ppb. The radii to the 5 selected concentration levels for each of the 13 size perc use groupings is given in Table 28.

In estimating exposure populations, it was assumed that all of the manufacturers are located in cities with 25,000 or more residents. The validity of this assumption is somewhat reinforced by the fact that no population exposures greater than 0.01 ppb are estimated for the four smallest plant size groups (see Table 28). The smaller manufacturing plants are more likely to be located in the smaller cities.

Census data were obtained on the 1970 population density of all cities with more than 25,000 residents. A uniform urban population density within each state was assumed.

C. Exposures

The number of people exposed to perc at annual average concentrations of 0.06-0.10, 0.11-1.00, and 1.01-4.00 ppb was estimated for each state on the bases of concentration radii given in Table 28, the urban population densities in the state, and the estimated number of plants in each of the 13 perc use groupings. The resulting estimates of population exposures to perc emissions from metal cleaning are given in

261<

Table 27

ESTIMATED PERC EMISSIONS FROM METAL CLEANING IN MANUFACTURING PLANTS OF VARIOUS SIZES

Perc Purchased* (gal/yr)	Estimated Assumed Perc Emissions (g/s)	Number of Plants†
10 - 29	0.003	47
30 - 59	0.009	37
60 - 99	0.015	98
100 - 299	0.029	254
300 - 599	0.087	645
600 - 799	0.136	122
800 - 999	0.174	225
1,000 - 2,999	0.291	409
3,000 - 5,999	0.872	175
6,000 - 7,999	1.356	90
8,000 - 9,999	1.744	0
10,000 - 29,999	3.875	231
30,000 - 59,000	8.718	0
60,000 - 79,999	13.562	7

---

*Purchased perc includes virgin and recycled perc as projected by the Eureka survey results.

†Estimated number of U.S. plants that use perc in degreasing.

Source: SRI estimates.

Table 29. It is estimated that 32 million people are annually exposed as a result of metal cleaning operations to atmospheric perc at concentrations of 0.05 to 4.0 ppb. The states in which more than 1 million people are exposed at these concentrations are California, Illinois, Michigan, New Jersey, New York, Ohio, and Pennsylvania.

Table 29

ESTIMATED POPULATION EXPOSURES TO ATMOSPHERIC PERC EMISSIONS FROM INDUSTRIAL DEGREASING

State	Population* Exposed to Perc (ppb)†		
	0.06-0.10	0.11-1.00	1.01-4.00
Alabama	150,000	88,000	270
Alaska	0	0	0
Arizona	4,600	1,500	0
Arkansas	32,000	18,000	50
California	3,500,000	2,100,000	42,000
Colorado	71,000	40,000	100
Connecticut	700,000	410,000	5,100
Delaware	0	0	0
District of Columbia	0	0	0
Florida	130,000	76,000	230
Georgia	120,000	69,000	220
Hawaii	0	0	0
Idaho	0	0	0
Illinois	2,700,000	1,600,000	15,000
Indiana	570,000	340,000	4,800
Iowa	31,000	17,000	50
Kansas	130,000	82,000	260
Kentucky	170,000	93,000	230
Louisiana	6,600	2,100	0
Maine	420	0	0
Maryland	180,000	94,000	200
Massachusetts	370,000	200,000	500
Michigan	1,600,000	96,000	9,800
Minnesota	180,000	100,000	240
Mississippi	5,400	1,800	0
Missouri	120,000	71,000	190
Montana	0	0	0
Nebraska	12,000	5,700	0
Nevada	0	0	0
New Hampshire	230	0	0
New Jersey	1,500,000	880,000	13,000
New Mexico	0	0	0
New York	2,400,000	1,400,000	3,700
North Carolina	77,000	43,000	120
North Dakota	0	0	0
Ohio	1,700,000	960,000	2,700
Oklahoma	25,000	14,000	40
Oregon	105,000	60,000	170
Pennsylvania	3,200,000	1,900,000	18,000
Rhode Island	97,000	51,000	100
South Carolina	32,000	18,000	40
South Dakota	0	0	0
Tennessee	66,000	38,000	110

Table 29 Continued

State	Population Exposed* to Perc (ppb)†		
	0.06-0.10	0.11-1.00	1.01-4.00
Texas	290,000	160,000	430
Utah	0	0	0
Vermont	0	0	0
Virginia	8,600	3,600	0
Washington	130,00	80,000	250
West Virginia	0	0	0
Wisconsin	55,000	32,000	90
Wyoming	0	0	0
U.S. Total	20,000,000	11,000,000	120,000

---

*Rounded to two significant figures.

†Annual average concentrations; to convert to 8-hour worst case, multiply by 25; to convert to $\mu g/m^3$, multiply by 6.7.

Source: SRI estimates.

266<

BIBLIOGRAPHY

1. Appleby, Alan, "Atmospheric Freons and Halogenated Compounds," Rutgers University, report to the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, NTIS PB-262 432, pp. 10-12, 107-127, 264-271 (November 1976).

2. Battelle-Columbus Laboratories, "Determination and Evaluation of Environmental Levels of Methyl Chloroform and Trichloroethylene," report to the U.S. Environmental Protection Agency (March 1977).

3. Dilling, W. L., N. B. Tefertiller, and G. J. Kallos, "Evaporation Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Chlorinated Compounds in Dilute Aqueous Solutions," Environmental Science and Technology, Vol. 9, No. 9, pp. 833-838 (September 1975).

4. Dusoleil, S., P. Goldfinger, A. M. Malieu-Van der Auwera, G. Martens, and D. Van Der Auwera, Trans Faraday Society, Vol. 57, p. 2197 (1961).

5. Evatovich, Mark, San Diego Air Pollution Control District, personal communication, San Diego, California (October 1978).

6. Fisher, William E., International Fabricare Institute, Research Division, Silver Spring, Maryland, paper presented at the EPA Hydrocarbon Control Workshop, Chicago, Illinois (20 July 1977).

7. Franklin Institute Research Laboratories, "Preliminary Study of Selected Potential Environmental Contaminants," report to the U.S. Environmental Protection Agency, NTIS No. PB-243 910 (July 1975).

8. Fuller, B. B., "Air pollution Assessment of Tetrachloroethylene," Mitre Corporation, report to the U.S. Environmental Protection Agency, Contract No. 68-02-1495 (February 1976).

9. Goldfinger, P., G. Huybrechts, and G. Martens, Trans Faraday Society, Vol. 57, p. 2210 (1961).

10. Greer, Jack K., Jr., Pollutant Strategies Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, personal communication (December 1978).

11. Hawley, G. E. (editor), The Condensed Chemical Dictionary, Van Nostrand Reinhold Company, Ninth Edition (1977).

12. Horowitz, A., and L. A. Rajbenback, Journal of the American Chemical Society, Vol. 9, p. 4105 (1968).

267<

13. Huybrechts, J., T. Olbrechts, and K. Thomas, Trans Faraday Society, Vol. 63, p. 1647 (1967).

14. International Fabricare Institute, "Dry Cleaning Solvent Emissions in the State of California 1974-1975," Joliet, Illinois (June 1975).

15. Kleeberg, Charles, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, personal communication (October 1978).

16. Kuriyang, T., Chemical Abstracts, Vol. 67 (1967).

17. Lapp, Thomas W., Betty L. Herndon, Charles E. Mumma, and Arthur D. Tippit, "An Assessment of the Need for Limitations on Trichloroethylene, Methyl Chloroform, and Perchloroethylene," draft final report to the Office of Toxic Substances, U. S. Environmental Protection Agency, Contract 68-01-4121, pp. 47-51, 133-135 (September 1977).

18. Leung, S., R. Johnson, C. S. Liu, G. Palo, R. Peter, and T. Tanton, "Alternatives to Organic Solvent Degreasing", Eureka Laboratories, Sacramento, CA, ARB A6-206-30 (May 1978a).

19. Leung, S., R. Johnson, C. S. Liu, G. Palo, R. Peter, and T. Tanton, "Alternatives to Organic Solvent Degreasing--Supplements," Eureka Laboratories, Sacramento, CA, ARB A6-206-30 (May 1978b)

20. Lillian, D., and H. B. Singh, "Absolute Determination of Atmospheric Halocarbons by Gas Phase Covlimetry," Analytical Chemistry, Vol. 46, No. 8, pp. 1060-1063 (1974).

21. Mara, Susan J., and Shonh S. Lee, "Assessment of Human Exposures to Atmospheric Benzene," SRI International, Menlo Park, California, report to the U.S. Environmental Protection Agency, NTIS No. PB 284 203/AS (May 1978).

22. Michigan Department of Public Health, Bureau of Environmental and Occupational Health, "Computer Listing of Dry Cleaners Licensed in the State of Michigan," Lansing, Michigan (November 1977).

23. Midwest Research Institute, "Test of Industrial Dry Cleaning Operations," draft final report, U.S. Environmental Protection Agency, Contract No. 68-02-1403 - Task 21 (April 1976a).

24. __________, "Source Test of a Dry Cleaner," draft final report, U.S. Environmental Protection Agency, Contract No. 68-02-1403 -- Task 23 (May 1976b).

25. Mitre Corporation, "Development of Standards of Performance for Solvent Metal Cleaning (Degreasing)," draft document prepared for the U.S. Environmental Protection Agency (July 1978).

26. Reid, F. H., and W. R. Halpin, Amer. Ind. Hygiene Assoc., Vol. 29, p. 390 (1968).

27. Scott Environmental Technology, Inc., "A Survey of Perchloroethylene Emissions from a Dry Cleaning Plant," report for the U.S. Environmental Protection Agency, No. 76-DRY-1, Research Triangle Park, North Carolina (March 1976).

28. Simmonds, P. G., S. L. Kerrin, J. E. Lovelock, and R. H. Shair, "Distribution of Atmospheric Halocarbons in the Air Over the Los Angeles Basin," Atmospheric Environment, Vol. 8, No. 3, pp. 209-216 (1974).

29. Suta, B. E., "BESTPOP: A Fine-Grained Computer System for the Assessment of Residential Population," SRI International, Menlo Park, California (1978).

30. Tuttle, T. C., G. D. Wood, C. B. Grether, and B. L. Johnson, "A Behavioral and Neurological Evaluation of Dry Cleaners Exposed to Perchloroethylene," report to the National Institute of Occupational Safety and Health, Center for Disease Control, Cincinnati, Ohio (June 1977).

31. U.S. Department of Commerce, Bureau of the Census, "County Business Patterns - 1970," CBP-70 Series, Government Printing Office, Washington, D.C. (December 1972).

32. __________, "1972 County and City Data Book," Government Printing Office, Washington, D.C. (1973).

33. __________, "County Business Patterns - 1974," CBP-74 Series, Government Printing Office, Washington, D.C. (December 1976).

34. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, "Monitoring for Perchloroethylene in Selected Cities," draft report (December 1978).

35. __________, Office of Air Quality Planning and Standards, "Control of Volatile Organic Emissions from Solvent Metal Cleaning," EPA-450/2-77-022 (November 1977).

36. Williams, I. H., Analytical Chemistry, Vol. 37, p. 1723 (1965).

269<

Appendix A

NUMBER OF DRY CLEANERS IN URBAN AREAS AND EXPOSED POPULATION FROM DRY CLEANERS, BY STATE

270<

Table A-1

ESTIMATED URBAN COMMERCIAL DRY CLEANERS THAT USE PERC, BY STATE

State	Number of Plants by Size of Operation (Employees)					Total Number of Plants
	1-4	5-9	10-19	20-49	50+	
Alabama	67	28	14	9	2	120
Alaska	1	1	—	1	2	5
Arizona	38	17	12	8	2	77
Arkansas	24	10	5	2	2	43
California	566	247	101	44	8	966
Colorado	62	35	13	10	1	121
Connecticut	65	29	14	17	1	126
Delaware	4	2	2	4	--	12
District of Columbia	38	26	15	5	1	85
Florida	106	71	27	27	5	236
Georgia	65	44	20	25	2	156
Hawaii	8	2	4	2	2	18
Idaho	8	3	2	1	--	14
Illinois	217	126	59	36	8	446
Indiana	82	41	18	14	5	160
Iowa	43	15	5	5	1	69
Kansas	50	17	4	4	--	75
Kentucky	32	18	5	9	4	68
Louisiana	75	29	14	6	2	126
Maine	3	1	1	5	—	10
Maryland	35	27	18	21	2	103
Massachusetts	128	64	34	21	5	252
Michigan	169	92	51	30	4	346
Minnesota	51	25	9	11	3	99
Mississippi	29	14	4	7	--	54
Missouri	96	35	18	9	2	160
Montana	8	3	1	2	—	14
Nebraska	21	12	5	4	2	44

Table A-1 (Concluded)

State	Number of Plants by Size of Operation (Employees) 1-4	5-9	10-19	20-49	50+	Total Number of Plants
Nevada	9	4	5	14	--	32
New Hampshire	7	3	1	2	—	13
New Jersey	163	58	21	23	2	267
New Mexico	19	7	5	2	—	33
New York	683	228	74	31	10	1,026
North Carolina	63	39	19	23	3	147
North Dakota	6	2	2	2	1	13
Ohio	198	107	47	41	7	400
Oklahoma	59	19	10	6	3	97
Oregon	31	11	2	5	—	49
Pennsylvania	126	68	36	45	7	282
Rhode Island	20	10	4	3	2	39
South Carolina	18	11	7	14	2	52
South Dakota	5	2	1	1	—	9
Tennessee	74	38	18	19	1	150
Texas	381	144	68	65	10	668
Utah	13	6	2	8	1	30
Vermont	2	--	1	--	—	3
Virginia	77	47	26	28	2	180
Washington	65	25	7	5	—	102
West Virginia	11	7	3	5	--	26
Wisconsin	69	34	11	10	2	126
Wyoming	4	2	1	--	--	7
Total U.S. Plants	4,194	1,906	846	691	119	7,756

Source: SRI estimates.

Table A-2

ESTIMATED URBAN COIN-OPERATED DRY CLEANERS THAT USE PERC, BY STATE

State	Number of Plants by Size of Operation (Employees) 1-4	5-9	10-19	20-49	50+	Total Number of Plants
Alabama	61	4	2	1	--	68
Alaska	4	1	--	--	--	5
Arizona	54	8	2	1	--	65
Arkansas	27	2	--	1	--	30
California	269	47	12	4	2	334
Colorado	59	8	2	--	1	70
Connecticut	33	6	2	--	--	41
Delaware	2	1	--	--	--	3
District of Columbia	25	5	1	--	--	31
Florida	195	20	3	2	1	221
Georgia	45	5	1	3	--	54
Hawaii	14	2	1	--	--	17
Idaho	9	1	--	--	--	10
Illinois	308	59	14	4	2	387
Indiana	138	32	5	1	--	176
Iowa	47	4	1	1	--	53
Kansas	50	6	2	--	--	58
Kentucky	46	6	--	--	1	53
Louisiana	37	2	1	2	--	42
Maine	6	2	--	--	--	8
Maryland	45	8	2	4	--	59
Massachusetts	83	10	5	3	--	101
Michigan	175	53	10	4	--	242
Minnesota	43	8	2	2	--	55
Mississippi	22	--	--	1	--	23
Missouri	90	14	4	1	--	109
Montana	7	2	--	--	--	9
Nebraska	18	2	1	--	--	21

Table A-2 (Concluded)

State	Number of Plants by Size of Operation (Employees) 1-4	5-9	10-19	20-49	50+	Total Number of Plants
Nevada	13	1	--	1	--	15
New Hampshire	11	1	--	--	--	12
New Jersey	83	8	2	2	1	96
New Mexico	29	3	--	--	--	32
New York	398	32	8	6	2	446
North Carolina	59	5	1	1	--	66
North Dakota	4	1	--	--	--	5
Ohio	209	42	9	3	--	263
Oklahoma	71	6	1	--	--	78
Oregon	22	4	2	--	--	28
Pennsylvania	109	13	5	2	1	130
Rhode Island	23	4	--	--	--	27
South Carolina	20	1	--	2	--	23
South Dakota	7	--	--	1	--	8
Tennessee	105	5	2	--	--	112
Texas	410	25	5	2	1	443
Utah	13	2	1	--	--	16
Vermont	2	--	--	--	--	2
Virginia	68	8	2	--	--	78
Washington	44	7	2	1	--	54
West Virginia	14	2	1	--	--	17
Wisconsin	64	11	5	1	--	81
Wyoming	5	--	--	--	--	5
Total U.S. Plants	3,695	499	119	57	12	4,382

Source: SRI estimates.

Table A-3

ESTIMATED URBAN INDUSTRIAL DRY CLEANERS THAT USE PERC, BY STATE

State	Number of Plants by Size of Operation (Employees)					Total Number of Plants
	1-4	5-9	10-19	20-49	50+	
Alabama	--	--	--	2	2	4
Alaska	--	--	--	--	--	--
Arizona	1	--	--	1	2	4
Arkansas	--	--	--	2	1	3
California	3	2	3	12	13	33
Colorado	1	--	1	1	1	4
Connecticut	--	--	--	1	1	2
Florida	--	1	1	4	6	12
Georgia	--	--	--	5	3	8
Illinois	1	--	--	5	7	13
Indiana	1	--	--	2	4	7
Iowa	--	--	--	2	2	4
Kansas	--	1	--	3	--	4
Kentucky	--	--	--	3	2	5
Louisiana	--	--	--	3	3	6
Maryland	--	--	--	--	3	3
Massachusetts	1	--	1	2	4	8
Michigan	1	--	2	6	5	14
Minnesota	1	1	--	1	1	4
Mississippi	--	--	--	1	1	2
Missouri	--	--	--	2	3	5
Nebraska	--	--	--	2	--	2
Nevada	--	--	--	1	--	1
New Hampshire	--	--	--	--	1	1
New Jersey	--	--	1	2	4	7
New Mexico	--	--	--	--	1	1
New York	2	3	2	7	6	20

Table A-3 (Concluded)

State	Number of Plants by Size of Operation (Employees)					Total
	1-4	5-9	10-19	20-49	50+	Number of Plants
North Carolina	--	--	--	6	4	10
Ohio	2	1	2	3	6	14
Oklahoma	--	--	--	2	1	3
Oregon	--	--	1	1	--	2
Pennsylvania	1	--	1	3	7	12
South Carolina	--	--	--	2	2	4
Tennessee	--	--	1	--	--	1
Texas	1	2	2	6	11	22
Virginia	--	--	--	1	3	4
Washington	--	--	--	3	--	3
West Virginia	--	--	--	--	1	1
Wisconsin	--	--	--	1	1	2
Total U.S. Plants	16	11	18	98	112	255

Source: SRI estimates.

Table A-4

ESTIMATED POPULATION EXPOSED TO PERC FROM COMMERCIAL DRY CLEANERS IN URBAN AREAS

State	Population Exposed*to Perc (ppb)**			Total Exposed Population*
	0.06-0.10	0.11-1.00	1.01-4.00	
Alabama	110,000	61,000	300	170,000
Alaska	45,000	27,000	400	72,000
Arizona	110,000	60,000	300	170,000
Arkansas	55,000	30,000	300	85,000
California	1,500,000	770,000	2,400	2,300,000
Colorado	240,000	120,000	300	360,000
Connecticut	210,000	110,000	200	320,000
Delaware	74,000	44,000	--	120,000
District of Columbia	500,000	260,000	900	760,000
Florida	290,000	160,000	700	450,000
Georgia	330,000	180,000	400	510,000
Hawaii	59,000	34,000	400	93,000
Idaho	16,000	8,000	--	24,000
Illinois	1,800,000	970,000	4,300	2,800,000
Indiana	270,000	150,000	1,000	420,000
Iowa	60,000	31,000	100	91,000
Kansas	61,000	29,000	--	90,000
Kentucky	290,000	160,000	1,400	450,000
Louisiana	170,000	84,000	400	250,000
Maine	20,000	12,000	—	32,000
Maryland	750,000	430,000	1,200	1,200,000
Massachusetts	540,000	290,000	1,400	830,000
Michigan	920,000	490,000	1,500	1,400,000
Minnesota	220,000	120,000	700	340,000
Mississippi	68,000	36,000	--	100,000
Missouri	180,000	94,000	400	270,000
Montana	29,000	15,000	--	44,000

Table A-4 (Concluded)

State	Population Exposed* to Perc (ppb)** 0.06-0.10	0.11-1.00	1.01-4.00	Total Exposed Population*
Nebraska	120,000	67,000	500	190,000
Nevada	78,000	47,000	--	130,000
New Hampshire	9,800	5,400	--	15,000
New Jersey	890,000	460,000	1,100	1,400,000
New Mexico	280,000	140,000	--	420,000
New York	4,700,000	2,200,000	10,000	6,900,000
North Carolina	280,000	160,000	600	440,000
North Dakota	55,000	32,000	300	87,000
Ohio	1,100,000	600,000	2,400	1,700,000
Oklahoma	44,000	24,000	200	68,000
Oregon	70,000	36,000	--	110,000
Pennsylvania	1,900,000	1,100,000	4,400	3,000,000
Rhode Island	130,000	69,000	600	200,000
South Carolina	110,000	62,000	300	170,000
South Dakota	13,000	6,700	--	20,000
Tennessee	130,000	69,000	100	200,000
Texas	800,000	430,000	1,600	1,200,000
Utah	84,000	49,000	200	130,000
Vermont	3,800	1,800	--	5,600
Virginia	200,000	110,000	200	310,000
Washington	110,000	51,000	--	160,000
West Virginia	55,000	31,000	--	86,000
Wisconsin	220,000	120,000	600	430,000
Wyoming	7,200	3,100	--	10,000
Total Exposed*	20,000,000	11,000,000	41,000	31,000,000

Source: SRI estimates.

*Rounded to two significant figures.

**Annual average concentrations; to convert to $\mu g/m^3$, multiply by 6.7; to convert to 8-hour worst case, multiply by 25.

Table A-5

ESTIMATED POPULATION EXPOSED TO PERC FROM COIN-OPERATED DRY CLEANERS IN URBAN AREAS

State	Population Exposed*to Perc (ppb)**			Total Exposed Population*
	0.06-0.10	0.11-1.00	1.01-4.00	
Alabama	13,000	3,200	--	16,000
Alaska	1.200	200	--	1,400
Arizona	15,000	4,200	--	19,000
Arkansas	7,000	2,100	--	9,100
California	180,000	61,000	--	240,000
Colorado	40,000	14,000	--	54,000
Connecticut	11,000	2,600	--	14,000
Delaware	1,800	400	--	2,200
District of Columbia	33,000	7,000	--	40,000
Florida	44,000	12,000	--	56,000
Georgia	26,000	9,800	--	36,000
Hawaii	4,300	1,100	--	5,400
Idaho	1,900	200	--	2,100
Illinois	360,000	120,000	--	480,000
Indiana	47,000	12,000	--	69,000
Iowa	11,000	2,800	--	14,000
Kansas	13,000	2,500	--	16,000
Kentucky	37,000	13,000	--	50,000
Louisiana	18,000	6,700	--	25,000
Maine	1,000	200	--	1,200
Maryland	93,000	39,000	--	132,000
Massachusetts	52,000	18,000	--	70,000
Michigan	150,000	49,000	--	200,000
Minnesota	27,000	9,700	--	37,000
Mississippi	7,000	2,200	--	9,200
Missouri	30,000	7,700	--	38,000
Montana	3,000	500	--	3,500

Table A-5 (Concluded)

State	Population Exposed*to Perc (ppb)** 0.06-0.10	0.11-1.00	1.01-4.00	Total Exposed Population*
Nebraska	7,100	1,500	--	3,500
Nevada	4,800	1,900	--	6,700
New Hampshire	1,100	90	--	1,200
New Jersey	110,000	39,000	--	150,000
New Mexico	4,700	400	--	5,100
New York	700,000	200,000	--	900,000
North Carolina	16,000	3,800	--	20,000
North Dakota	1,600	200	--	2,000
Ohio	140,000	38,000	--	180,000
Oklahoma	4,700	500	--	5,200
Oregon	10,000	2,900	--	13,000
Pennsylvania	160,000	55,000	--	220,000
Rhode Island	8,900	1,100	--	10,000
South Carolina	8,100	3,400	--	12,000
South Dakota	5,700	2,600	--	8,300
Tennessee	12,000	1,300	--	13,000
Texas	84,000	16,000	--	100,000
Utah	4,400	1,100	--	5,500
Vermont	400	--	--	400
Virginia	10,000	1,700	--	12,000
Washington	22,000	6,600	--	29,000
West Virginia	5,200	1,300	--	6,500
Wisconsin	35,000	11,000	--	46,000
Wyoming	1,100	--	--	1,100
Total Exposed*	2,600,000	790,000	--	3,400,000

Source: SRI estimates.

*Rounded off to two significant figures.

**Annual average concentrations; to convert to $\mu g/m^3$, multiply by 6.7; to convert to 8-hour worst case, multiply by 25.

Table A-6

ESTIMATED POPULATION EXPOSED TO PERC FROM INDUSTRIAL DRY CLEANERS IN URBAN AREAS

State	Population Exposed*to Perc (ppb)** 0.06-0.10	0.11-1.00	1.01-4.00	Total Exposed Population*
Alabama	22,000	13,000	30	35,000
Arizona	21,000	13,000	30	34,000
Arkansas	15,000	9,100	20	24,000
California	320,000	200,000	400	520,000
Colorado	27,000	15,000	30	72,000
Connecticut	16,000	9,900	20	26,000
Florida	62,000	37,000	90	99,000
Georgia	61,000	38,000	70	99,000
Illinois	300,000	170,000	400	470,000
Indiana	53,000	33,000	90	86,000
Iowa	22,000	14,000	30	36,000
Kansas	14,000	7,500	--	22,000
Kentucky	63,000	39,000	80	100,000
Louisiana	52,000	32,000	70	84,000
Maryland	100,000	66,000	200	170,000
Massachusetts	79,000	47,000	100	130,000
Michigan	160,000	94,000	200	250,000
Minnesota	21,000	12,000	30	33,000
Mississippi	14,000	9,000	20	23,000
Missouri	41,000	26,000	60	67,000
Nebraska	12,000	7,000	—	19,000
Nevada	3,100	1,800	--	4,900
New Hampshire	5,600	3,600	10	9,200
New Jersey	150,000	93,000	200	240,000
New Mexico	8,900	5,700	20	15,000
New York	540,000	310,000	700	850,000
North Carolina	67,000	41,000	80	110,000
Ohio	150,000	88,000	200	240,000

Table A-6 (Concluded)

State	Population Exposed*to Perc (ppb)**			Total Exposed Population*
	0.06-0.10	0.11-1.00	1.01-4.00	
Oklahoma	6,100	3,700	10	9,800
Oregon	8,600	3,300	--	12,000
Pennsylvania	300,000	180,000	500	480,000
South Carolina	21,000	13,000	30	34,000
Tennessee	1,200	--	—	1,200
Texas	130,000	78,000	200	210,000
Virginia	23,000	14,000	40	37,000
Washington	17,000	9,800	--	27,000
West Virginia	13,000	8,100	30	21,000
Wisconsin	20,000	13,000	30	33,000
Total Exposed*	2,900,000	1,800,000	4,000	4,700,000

Source: SRI estimates.

*Rounded off to two significant figures.

**Annual average concentrations; to convert to $\mu g/m^3$, multiply by 6.7; to convert to 8-hour worst case, multiply by 25.